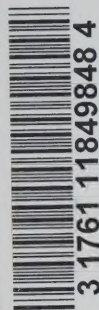


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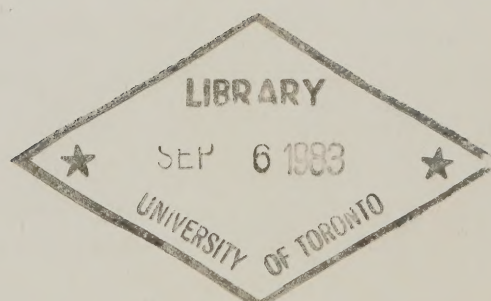
Royal Commission on Matters of Health
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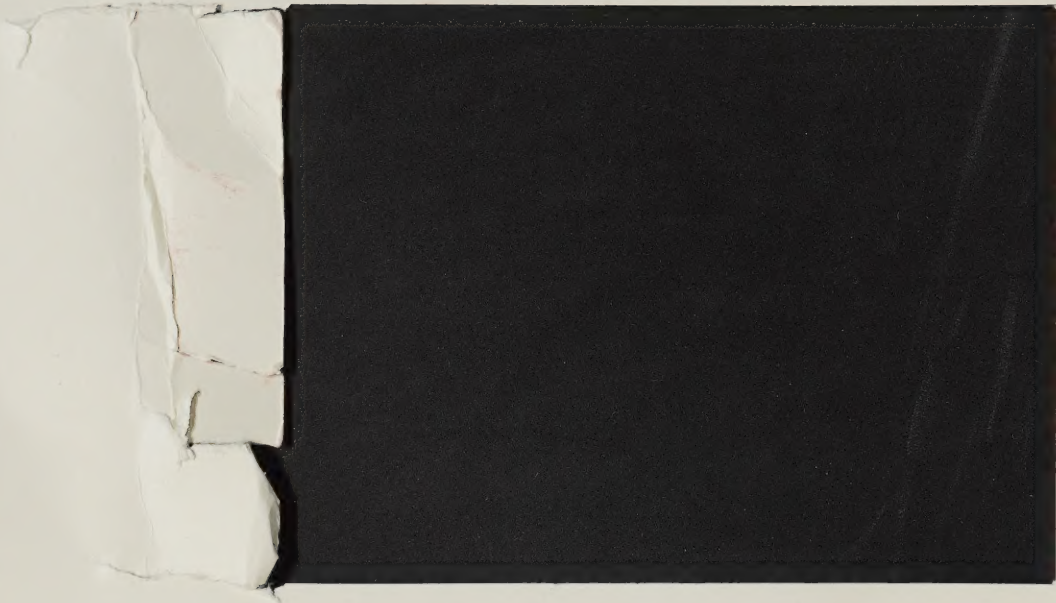
MEASUREMENT OF ASBESTOS FIBRE
CONCENTRATIONS IN AMBIENT ATMOSPHERES

A Study Prepared By:

Dr. Eric J. Chatfield
Ontario Research Foundation

Study Series





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for


The Royal Commission on Matters of Health and Safety

Arising from the Use of Asbestos in Ontario

* * * * *

This study was commissioned by the Royal Commission on Asbestos, but the views expressed herein are those of the author and do not necessarily reflect the views of the members of the Commission or its staff.

May 1983



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MEASUREMENT OF ASBESTOS FIBRE CONCENTRATIONS
IN AMBIENT ATMOSPHERES

A Study Prepared By:

Dr. E.J. Chatfield
Manager, Electron Optics Centre
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario, Canada L5K 1B3

for

The Royal Commission on Matters of Health and Safety
Arising from the Use of Asbestos in Ontario

May 1983

MEMORANDUM OF ASSOCIATION
IN ANTI-COMMUNISM

A study prepared by

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PREFACE

This document contains a review of the methods for measurement of asbestos fibres in ambient atmospheres, and the characteristics of these methods are discussed in detail. Procedures for identification of asbestos fibres are also reviewed. The published literature on the concentrations of asbestos fibres in ambient atmospheres is compared with recent measurements made in Ontario. Measurements made in closed environments such as buildings and subway systems are also considered. Recommendations are made concerning analytical methods, interpretation and future research needs.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

This paper considers in detail the characteristics of the various types of asbestos, and what instrumental methods can be used to identify and measure single microscopic fibres which may be present in ambient atmospheres. Several different methods of sample preparation for transmission electron microscopy are reviewed, and a complete protocol for identification of asbestos fibres is specified. Published measurements of asbestos fibre concentrations in ambient air, building atmospheres and subway transit atmospheres are examined critically, and new data are presented. Unresolved problems in the analytical procedures are considered, and a number of recommendations are made concerning analytical procedures and interpretation of results.

The adverse health effects produced by inhalation of asbestos fibres have been extensively documented (80, 53). Results of various studies so far reported indicate that the carcinogenic potential of an asbestos fibre is likely to be related to its dimensions (88, 65), and there is strong evidence that in both animals and humans some varieties of fibre are more carcinogenic than others (37, 91, 2). It has also been suggested that the surface chemistry of the fibre is an additional relevant factor (33). It has not so far been possible to demonstrate that a lower "threshold" level of airborne fibre concentration exists below which no asbestos-related diseases occur (1). Consequently, the presence of low levels of airborne asbestos fibres in the general environment (58, 42, 82, 78, 14, 86, 94) has led to speculation that these may pose some cancer risk to the general population (98, 56, 15). Further interest in the possible effects of low-level or short-term non-occupational exposures developed with the discovery that some family contacts of asbestos workers began to show signs of asbestos-related disease (4, 55).

In the general environment, airborne asbestos fibres comprise a very small minority of the total number of particles. Moreover, the types of fibres which may be present are unknown, and each fibre must be

identified. Also, the diameters of asbestos fibres found in the general environment are usually very small, below the minimum which can be detected by optical microscopy. All of these aspects of the measurement problem are different from those which relate to workplace atmosphere measurements in which most fibres are known to be asbestos and many are detectable by optical microscopy.

Transmission electron microscopy (TEM) is the preferred method of analysis for environmental measurements, but techniques used to convert the sample collection filter into a TEM specimen have varied between investigators. Some of these techniques incur large and unreproducible losses of fibres, and others are sensitive to low levels of contamination sometimes present in the sample collection filter. It is also claimed that some techniques cause high fibre counts to be reported because particular steps in the specimen preparation fragment large fibres into greater numbers of smaller ones.

The fibre definition used in occupational fibre counts clearly specifies limits on the fibre dimensions, and it is accepted that a fibre count based on this restricted range of fibre dimensions represents only an index of exposure which can be compared with a legislated standard. In contrast, no limits have yet been placed on the dimensions of fibres which should be incorporated in an environmental fibre count. The medical community has been unable to agree on the minimum size of fibre which the analyst should attempt to measure and identify. Selikoff and Lee have concluded that there is no evidence to discount the possibility that adverse health effects may result from inhalation of fibres shorter than 5 micrometres (μm) (81). This opinion is consistent with the Pott model (65, 64). This model assigns a continuous scale of carcinogenic potency, which is a function of both diameter and length, and includes fibres not incorporated in occupational fibre counts. Pott considers that a large number of short fibres may induce a tumour as effectively as a few long fibres. However, the relative importance of long and short fibres

is still a matter of some controversy.

The discharge of asbestos fibres into the environment is not confined to mining and processing of asbestos. Products which contain asbestos, such as asbestos-cement and brake linings, erode or wear in use and some of the material becomes airborne. Asbestos fibres also often occur in low concentrations mixed with other minerals, for example in talc, iron ores and vermiculite. Chrysotile asbestos is present in many areas of the world, but not often in commercially-viable concentrations (67). Nevertheless, if mined for other purposes, these minerals may pose an environmental hazard to the general population. In the U.S.A., crushed serpentine rock containing a small proportion of chrysotile was used as unpaved road construction material (94). A similar example of this use of serpentine rock has been reported by Spurny and Stoher (86). In another quarry producing rock for the same purpose, veins of fibres were found which were identified as actinolite (85), and animal experiments showed these actinolite fibres to be carcinogenic like other asbestos minerals.

Some fibrous minerals other than asbestos have been shown to be carcinogenic. In particular, the fibrous zeolite erionite is thought to induce mesothelioma (11), and animal experiments have shown that the fibrous clay attapulgite can produce mesothelioma after intraperitoneal injection (66). Therefore, in analyses of ambient air it is not sufficient to account for only those fibres which can be identified as belonging to one of the common asbestos varieties. Ambient air may contain fibres from a number of different sources; most of these fibres are usually not asbestos and identification of some may be difficult.

In view of the uncertainties about the relative significance of different fibre sizes and fibre types, it is clear that analytical methods for determination of mineral fibres in ambient air must be capable of both measurement and identification of all fibres which have dimensions within the ranges thought to be of biological

significance. The minimum concentration of airborne fibres which is of concern is also uncertain, but to some extent the detection limit is imposed by the analytical method. It was recently agreed by a working group of the International Organization for Standardization (ISO) that the analytical method for determination of asbestos in ambient air should be designed to detect a concentration of 1 fibre/litre in urban atmospheres, and 0.1 fibre/litre in remote rural locations (40).

Published ambient air measurements have been obtained using a variety of analytical techniques during a period when both instrumentation and techniques were being improved rapidly, and it is therefore difficult to compare the results reported by different investigators. Because some techniques used were either known or thought to cause fragmentation of large fibres, results have often been quoted only in terms of mass concentrations, making comparisons even more difficult. Some new measurements of ambient air fibre concentrations in Ontario are reported, and the significance of the analytical procedures and reporting methods are discussed. A number of unresolved problems in ambient air analysis can still be defined.

2. MINERALOGICAL ASPECTS

In order to appreciate the analytical sophistication required for identification of asbestos fibres, it is important to understand the meaning of the term "asbestos" and also the chemical properties of the various types.

Asbestos is a collective term used to describe several hydrated silicate minerals which have the property that they can be separated into long, thin fibres. Figure 1 shows the most common varieties of asbestos. The majority of the asbestos in commercial use is chrysotile, the fibrous variety of serpentine which has the theoretical composition $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$. The silicon may be partially substituted by aluminium, and magnesium may be partially substituted by iron, nickel, manganese, zinc or cobalt (96). In material from some sources there are embedded particles of magnetite in the fibres. Chrysotile has an unusual structure, and consists of parallel sheets of silicon tetrahedra and magnesium octahedra. There is a dimensional misfit between the two sheets, which gives rise to a curved cylindrical structure in the form of a scroll. In the other varieties of serpentine, lizardite and antigorite, the dimensional misfit is accommodated in different ways and gives rise to two other types of structure. The detailed structures of the serpentines have been described by Wicks (96).

The other types of asbestos are the fibrous varieties of amphibole minerals. These are ferro-magnesian silicates of the general formula $\text{A}_{2-3} \text{B}_5 (\text{Si}, \text{Al})_8 \text{O}_{22} (\text{OH})_2$ where $\text{A} = \text{Mg}, \text{Fe}^{+2}, \text{Ca}, \text{Na}$ or K , and $\text{B} = \text{Mg}, \text{Fe}^{+2}, \text{Fe}^{+3}$ or Al . Some of these elements may also be partially substituted by $\text{Mn}, \text{Cr}, \text{Li}, \text{Pb}, \text{Ti}$ or Zn . The amphiboles all have similar crystal structures, characterized by a cross-linked double chain of silicon tetrahedra with a silicon:oxygen ratio of 4:11 (95). The definition of mineral species within the wide compositional range of the amphiboles has been considered by a committee of the International Mineralogical Association, and a classification system

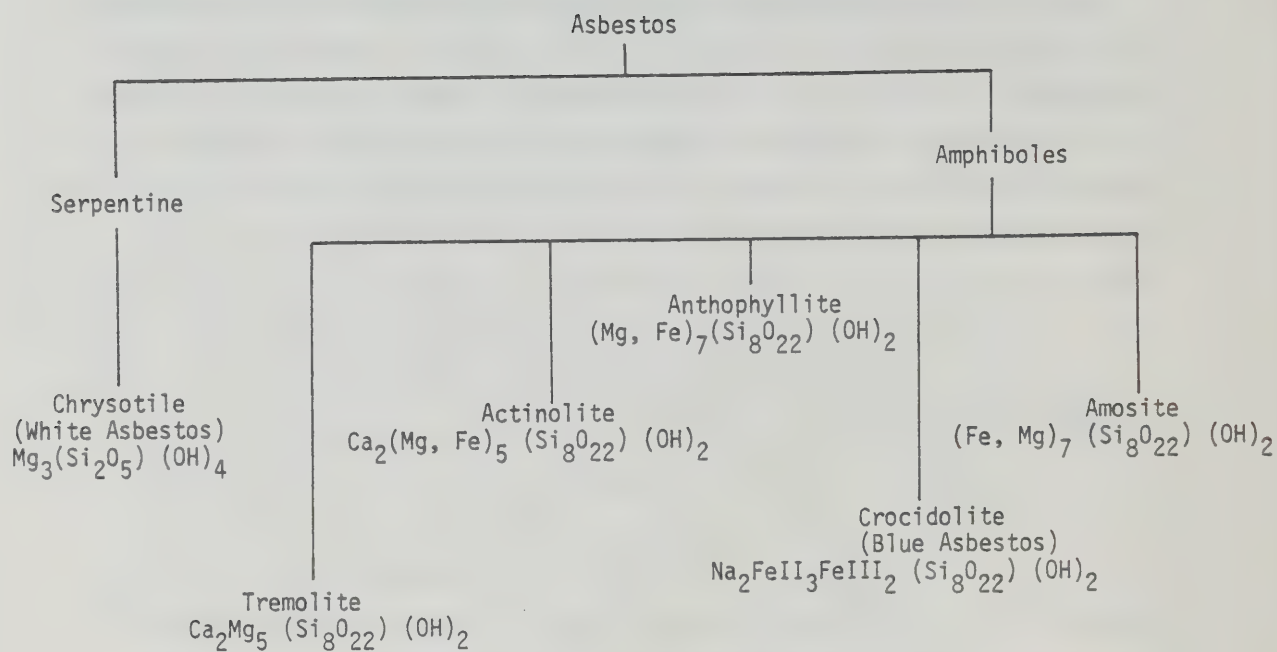


Figure 1. Varieties of asbestos.

has been developed (38). In Figure 1, the common commercially-used amphibole asbestos types are crocidolite (blue asbestos) and amosite (brown asbestos). Amosite is not a correct mineralogical term; it was derived from a trade name "Amosa", an acronym for Asbestos Mines of South Africa. Amosite is composed of cummingtonite and grunerite, with some tremolite or actinolite. Anthophyllite is now rarely used commercially.

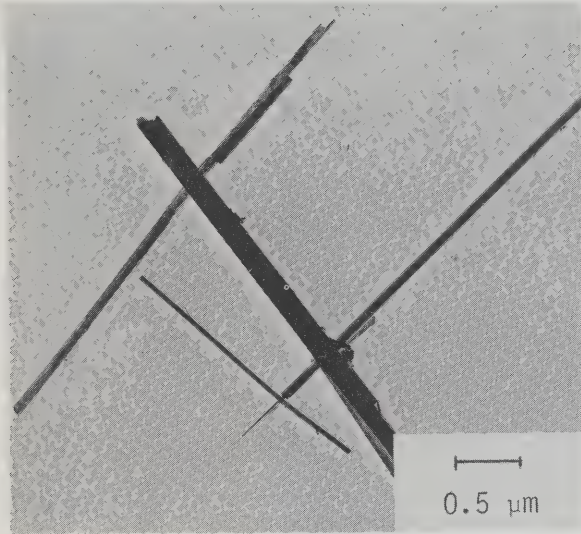
It is commonly thought that the asbestos minerals are indestructible: in fact all of them are subject to both chemical attack and thermal degradation. Chrysotile is attacked readily by acids (84). The amphibole asbestoses are generally more resistant to acid attack, although there are some differences between varieties. Independently of the surrounding atmosphere, dehydroxylation of chrysotile occurs in the range 600 - 780 °C, and at 800 - 850 °C the anhydride breaks down to form forsterite and silica (36). Finely divided chrysotile samples have also been shown to dehydroxylate at much lower temperatures (13). The thermal decomposition of the amphiboles is more complex and depends on the nature of the surrounding atmosphere. The decomposition products often include pyroxenes, cristobalite and iron oxide. It should be recognized that both the chemical and thermal decomposition of asbestos may yield products which retain the fibrous morphology of the original mineral. Moreover, although these degradation products, consisting of finely divided mixtures of various phases, can no longer be classified as asbestos, the mean composition is similar to that of the original asbestos.

Identification of small particles of asbestos is complicated by the fact that for each of the varieties there is also a non-fibrous polytype or polymorph of similar or identical composition and basic crystal structure. Amphiboles have a very good cleavage along two sets of planes parallel to the crystallographic "c" axis, and this tends to produce elongated fragments when the materials are crushed. Since the current definition of a fibre is a particle with a length:width (aspect) ratio of 3:1 or greater, many of these fragments qualify as

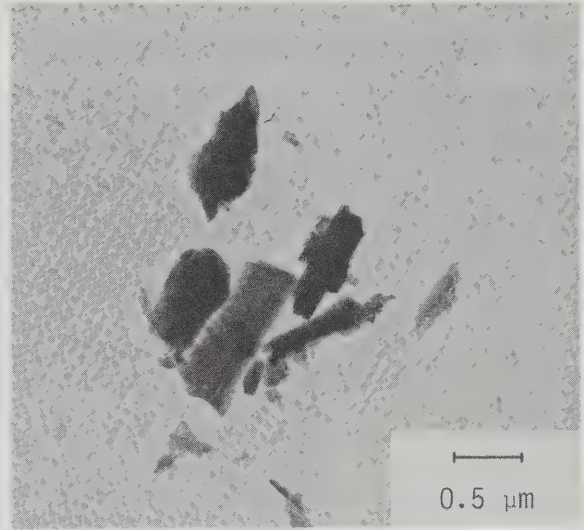
"fibres". The fundamental problem is that, although in a large specimen the mineral is perceived as obviously not fibrous, single microscopic particles of the mineral cannot easily be discriminated from those of similar dimensions which have originated from the asbestos variety. The discrimination problem becomes progressively more acute for smaller fragments or fibres. Moreover, to compound the problem further, the non-fibrous types are usually found associated with the asbestos variety. Campbell et al (16) have studied a number of these minerals, and have carefully defined the difference between fibres of the true asbestos varieties and cleavage fragments of the non-fibrous amphiboles.

Figure 2 shows electron micrographs of crocidolite and riebeckite. It is clear that this sample of crocidolite is fibrous, and that the riebeckite sample is non-fibrous. Nevertheless, there is little difference between either the chemical compositions or the crystal structures of the two minerals, and the ranges of aspect ratios in the two minerals overlap significantly. Similar comparisons can be made for amosite and grunerite. In the case of the serpentines, the chemical compositions of chrysotile, antigorite and lizardite are very similar, although in these minerals the crystal structures are different.

The question is still open as to whether cleavage fragments, like the true fibres, display carcinogenic potency, and is a matter of much controversy (71). McDonald et al (52) studied the workers in a hard rock mine who were exposed to cummingtonite-grunerite, and concluded that there was no excess of malignant diseases in the group. This result appeared to contradict those of an earlier study by Gillam et al (35), who found a significant excess risk of respiratory cancer. The interpretation of these studies is still controversial. A definitive conclusion from such a study would give guidance to the analyst as to whether the difficult discrimination in the microscope between cleavage fragments and fibres is necessary or meaningful.



CROCIDOLITE



RIEBECKITE

Figure 2. Transmission electron micrographs of crocidolite and riebeckite showing that this sample of crocidolite is fibrous and the sample of riebeckite is non-fibrous. These two minerals have similar chemical compositions and crystal structures, and the ranges of aspect ratios overlap.

Amphibole minerals are often found as contamination in other mineral products. Tremolite is often found in talc and chrysotile deposits, and actinolite is present in some vermiculite deposits. Figure 3 is an electron micrograph of a product which was originally marketed as "fibrous talc", but complete analysis indicated that mineralogically its structure and composition corresponded to those of anthophyllite. Figure 4 shows actinolite fibres found in one variety of vermiculite. These examples illustrate the requirement for critical selection of the criteria to be used for identification of single particles of the asbestos minerals.

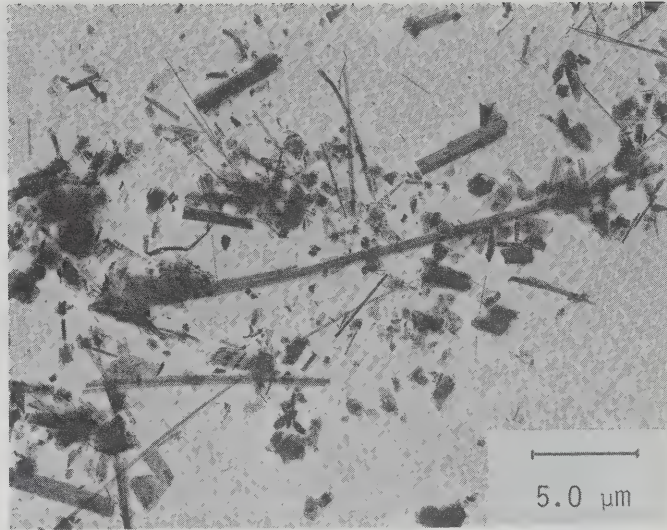


Figure 3. Transmission electron micrograph of a product marketed as "fibrous talc". Mineralogically its structure and composition correspond to those of anthophyllite.

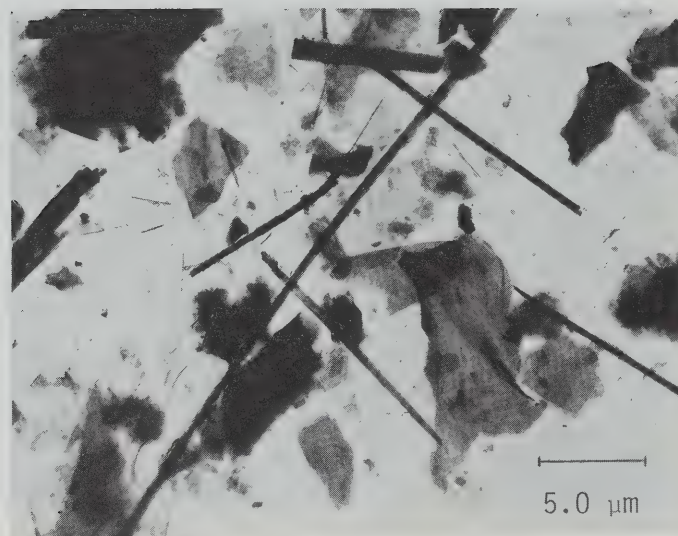


Figure 4. Transmission electron micrograph showing actinolite fibres found in a sample of vermiculite.

3. INSTRUMENTAL ANALYSIS METHODS

3.1 Phase Contrast Optical Microscopy

In workplace atmospheres, asbestos is monitored by the membrane filter method. There are several versions of this method (50, 59, 10, 39), which are all based on phase contrast optical microscopy (PCM). Using the best phase contrast optical microscope, fibres which have diameters below $0.2\ \mu\text{m}$ cannot be detected, regardless of their lengths (10, 49). If the optical microscope is not of the best quality, or if it is improperly aligned, the detection limit may be degraded to about $0.4\ \mu\text{m}$. Figure 5 shows a transmission electron micrograph of a single chrysotile fibril, superimposed on which are circles representing the minimum diameters of fibres which can be detected by PCM under both optimum and degraded conditions. It is clear that the utility of PCM depends on the proportion of the fibres which exceed about $0.2\ \mu\text{m}$ in diameter.

In the environment it is unusual to encounter the large fibre bundles which are found in the asbestos workplace atmosphere. Any asbestos in the general environment is usually present either as single fibrils or as randomly oriented aggregates of fibrils alone or attached to other particulate. Such single fibrils or aggregates are not detectable by optical microscopy because of the limited resolution of the PCM technique. In the diagram shown in Figure 6, the optically-visible proportion of the total number of fibres in a dispersion is represented by the shaded area.

It is instructive to examine a typical asbestos fibre length distribution in terms of the total number of fibres, those longer than $5\ \mu\text{m}$, and those which are visible by PCM. Unfortunately, the size distributions of asbestos fibres in ambient air have generally not been quoted in the literature. This is because in

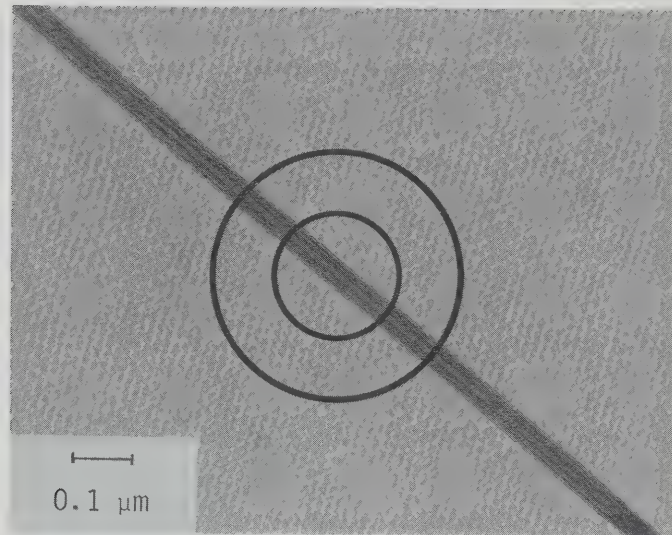


Figure 5. Transmission electron micrograph of a single fibril of chrysotile. Small circle represents limit of visibility ($0.2\text{ }\mu\text{m}$) using research optical microscope. Large circle represents limit of visibility ($0.4\text{ }\mu\text{m}$) using optical microscope with lower quality objective lens.

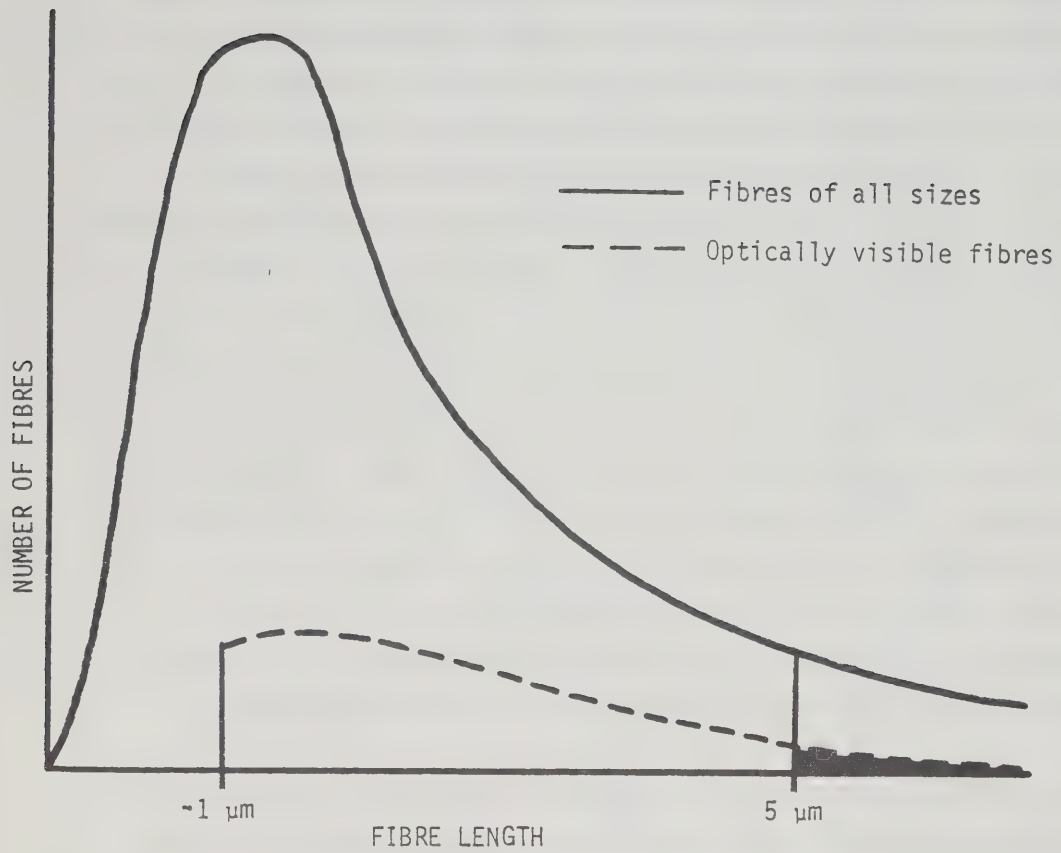


Figure 6. Relationship between total fibre distribution and optical fibre count. (Solid shaded area shows optical fibre count).

most of the environmental measurements there has been an emphasis on the number or mass of fibres found, rather than on their sizes, and the actual numbers of fibres counted were usually not adequate to establish statistically-reliable size distributions. An example of a statistically-valid fibre length distribution extending to fibres longer than 5 μm is shown in Figure 7, which can be used to illustrate the measurement problem. This fibre size distribution was obtained by combining data from analyses of four filters collected in the Stockholm Subway System in 1981. The most likely origin of these chrysotile asbestos fibres was from brake linings used on the trains, and in the relatively closed environment of the tunnels and stations there would be little opportunity for dilution or settling of the particulate to occur while trains were operating. In this dispersion, it can be seen that only 0.7% of the total number of fibres exceeded 5 μm in length. From the original fibre dimension data it was also determined that, of the fibres exceeding 5 μm in length, only about 50% had widths such that they would theoretically be optically-visible using PCM.

Since routine fibre counts by electron microscopy are usually terminated after 100 - 200 fibres have been counted, it can be seen from Figure 7 that, for this dispersion, such a procedure will on average allow detection of only 0.7 - 1.4 fibres longer than 5 μm . In contrast, the standard PCM methods used for workplace atmosphere measurements would be capable of detecting only about 3 chrysotile fibres of every thousand known to be present in this dispersion and the technique does not provide for any identification of the fibres.

In the PCM method no attempt is made to discriminate asbestos fibres from any other types of fibre, and although it is found that an optical fibre count made on an environmental sample usually yields a definite value, this value is totally unrelated to the presence or absence of any asbestos. The results of an

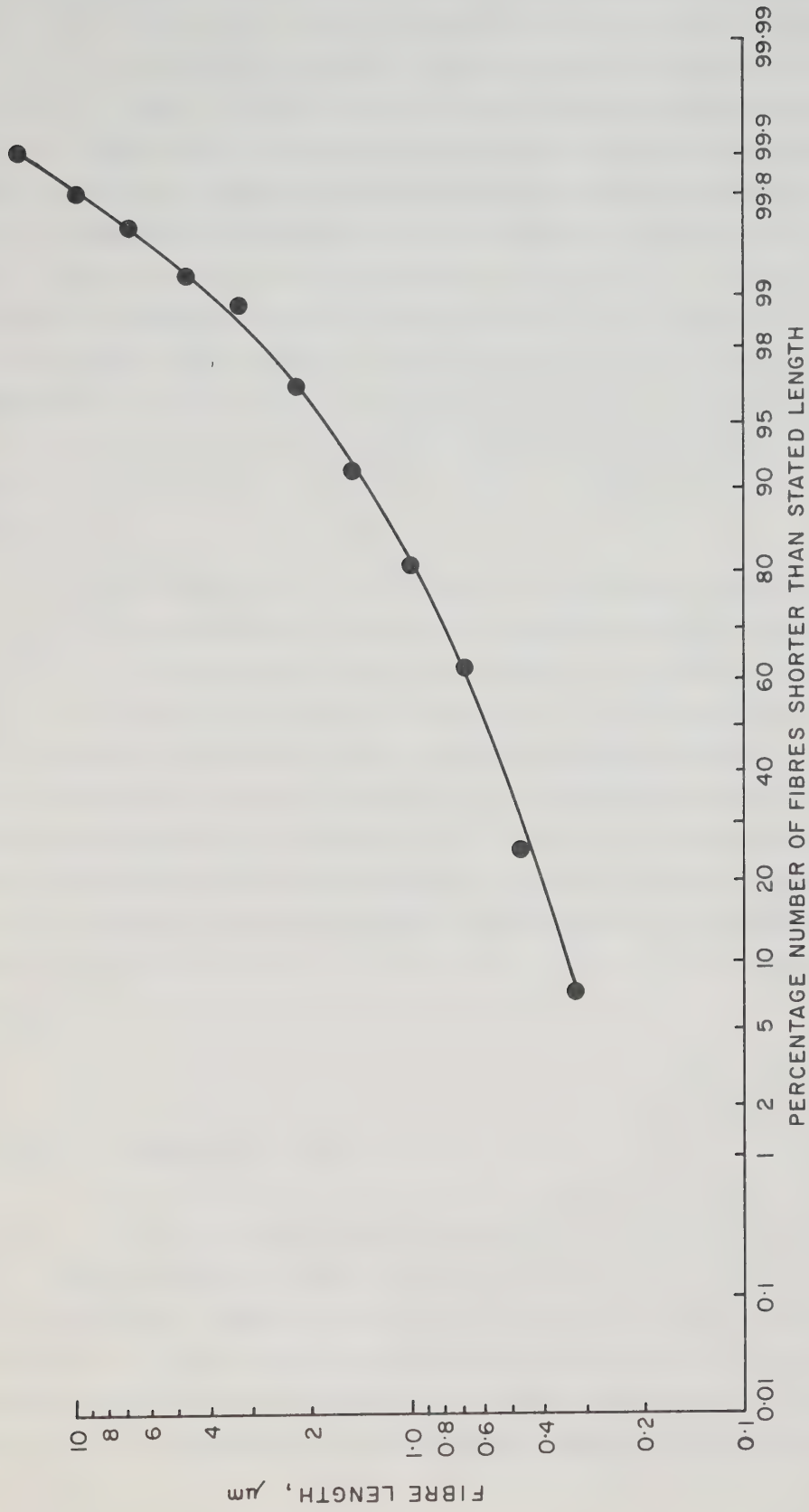


Figure 7. Stockholm Subway: Chrysotile fibre length distribution.

optical fibre count performed on a general environment sample can be challenged in two ways: if the result is low it does not give confidence that asbestos is not present, since any asbestos fibres would have diameters too small for detection; if the result is high, the argument can be introduced that few if any of the fibres were actually asbestos and that they were all some other "fibrous" species. It might be argued that the PCM should be used to determine environmental asbestos fibre concentrations because phase contrast optical fibre counts are the only ones for which reliable epidemiological data exist. However, since the fibres counted optically in an environmental sample are not usually asbestos, the argument to use PCM methods is difficult to support.

It is widely accepted that the PCM method is totally unsuitable for measurement of asbestos fibres in ambient atmospheres. The U.S. National Institute of Occupational Safety and Health recommends against the use of optical microscopy techniques for monitoring of ambient atmospheres (99). Many others also reject the use of PCM for environmental measurements, whether inside or outside buildings (78, 19, 42, 61, 47) and the U.S. Environmental Protection Agency have specified a method based on transmission electron microscopy (TEM) for asbestos measurements in ambient atmospheres (74).

Gibbs et al (34) have carried out parallel air sampling close to and remote from sources of airborne asbestos fibres. One of the sites chosen was adjacent to the tailings pile of an active asbestos mine, another site was in the town of Thetford Mines, Québec, which is surrounded by asbestos mining activity, and the third was at Mont St. Hilaire, Québec, remote from asbestos sources. On the basis of the optical microscopy data, the fibre concentrations at the two mining sites were statistically identical with those at the remote sampling point, which is not a plausible result. In contrast, the TEM data yielded high

concentration values up to 10000 ng/m³ at the two mining sites and values close to the detection limit of about 1 ng/m³ were obtained at the remote sampling point. The fact that the PCM analyses did not allow differentiation between these extremes of fibre concentration clearly indicates that the technique has no part to play in ambient air monitoring for asbestos fibres, and that results based on PCM evaluations should be discounted.

A number of authors have erroneously applied PCM techniques to the measurement of, asbestos fibre concentrations in ambient atmospheres, both indoors and outside (72, 45, 75, 9, 8, 92, 93). In all of these papers, analytical detection limits were claimed which are significantly below the stated values published in the method manuals (10, 50), namely 0.1 fibre/mL in optimum circumstances and perhaps as poor as 0.5 fibre/mL on heavily loaded filters. Indeed, in one of these studies (72) measurements of 0.0005 fibre/mL are quoted as meaningful. In studies on the emissions from vinyl floor coverings (92, 93), the authors converted the PCM fibre counts to asbestos fibre counts. This was achieved by taking into account the subjective opinion of the microscopist as to what proportion of the total fibres were asbestos, despite the absence of any reliable technique capable of achieving this discrimination. This somewhat questionable procedure was carried out on PCM results, most of which were already at or below the published detection limit.

3.2 Scanning Electron Microscopy

A modern scanning electron microscope (SEM) has an instrumental resolution of about 5 nanometres (nm) (1 nm = 10⁻⁹m). It is possible to interface with this instrument an energy dispersive X-ray analyzer (EDXA), which permits X-ray spectra to be obtained from individual small particles. The X-ray spectrum obtained is characteristic of the chemical composition of the

particle. The resolution of about 5 nm would seem to be adequate for reliable detection of the smallest fibrils of chrysotile, which are usually 30 - 40 nm in diameter. The instrumental resolution is usually demonstrated using micrographs of relatively ideal samples. In order to obtain the best resolution, it is necessary to work using low electron beam currents, and this requirement results in an image which contains a significant component of electrical noise. Accordingly, the test resolution micrographs are obtained by using long exposure times so that the noise component is averaged, and it is then largely eliminated from the photographic image. These operating conditions, however, are not realistic for routine fibre counting using a real time image, and higher beam currents must be used to allow a noise-free image to be obtained. Quite separately from the question of instrumental resolution, the specimen itself also imposes resolution and contrast limitations.

For SEM fibre counting, the particulate sample is collected on a Nuclepore polycarbonate filter which is then coated with carbon to make the sample surface electrically conducting. In the SEM image, it is found that thin fibres and flat platy particles display poor contrast (25) and consequently may not be detected. Moreover, it is possible to discount some thin fibres as artifacts of the filter surface. The lack of any method for specific fibre identification is a major limitation of analytical methods based on the use of the SEM (73, 25, 19). It is not possible, for example, to discriminate reliably and routinely between elongated particles of talc, anthophyllite, chrysotile, antigorite and lizardite. A method based on the use of a gold-coated Nuclepore filter has been described (44). The gold-coated filter is used for sample collection, and organic particles are oxidized by exposure of the filter in a low temperature plasma asher. The filter is examined in the SEM, and fibres are identified on the basis of their EDXA spectra. Unfortunately, one of the EDXA peaks from gold occurs at 1.66 keV

which overlaps the silicon $K\alpha$ peak at 1.74 keV, and this leads to uncertainty in the identification of small diameter fibres.

It is clear that in general the resolution, contrast and fibre identification limitations of the SEM-EDXA system preclude its use for true environmental measurements where the fibres are usually of small diameters and neither the origins nor the species of fibres are known.

3.3 Transmission Electron Microscopy

A modern transmission electron microscope (TEM) has a resolution of about 0.2 nm, which is more than adequate for resolving unit fibrils of chrysotile. This resolution is readily achieved under normal operating conditions of the TEM. The image obtained also permits observation of some internal structure of the fibres. Figure 8 shows a very high magnification TEM image of a single chrysotile fibril. Characteristic features can be seen, in particular the tubular structure. Note the high magnification necessary to observe these features (about 100,000), and the clarity of the image. Some fibres are sensitive to the heating caused by electron beam irradiation, and morphological changes occur. Figure 9 shows the morphology of a chrysotile fibril after such degradation has taken place. Identification can be achieved using selected area electron diffraction (SAED), in which the electron diffraction pattern displayed by a single fibre can be inspected. This pattern is characteristic of the crystalline structure of the fibre. After prolonged examination in the TEM, it is often found that fibres of heat-sensitive minerals such as chrysotile become amorphous, after which they no longer display SAED patterns.

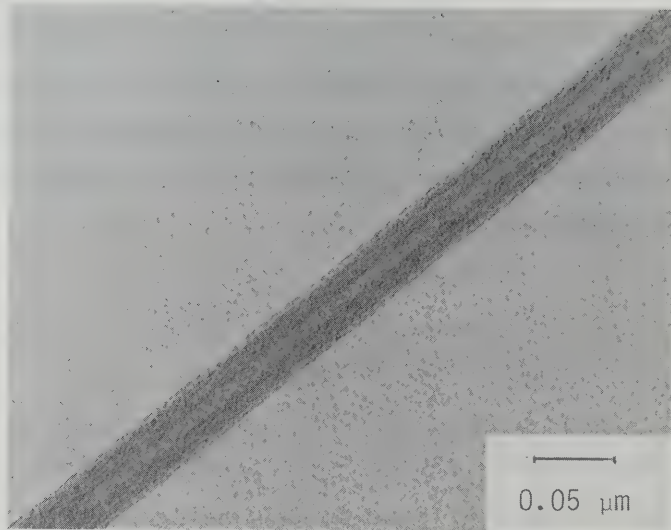


Figure 8. Transmission electron micrograph of chrysotile fibril, showing morphology.

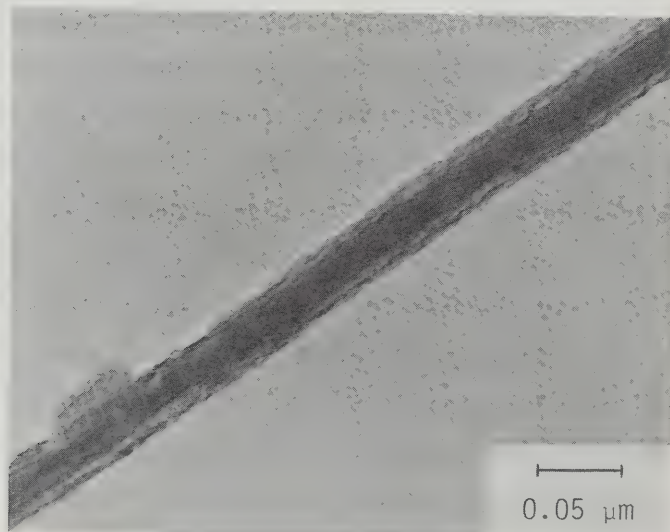


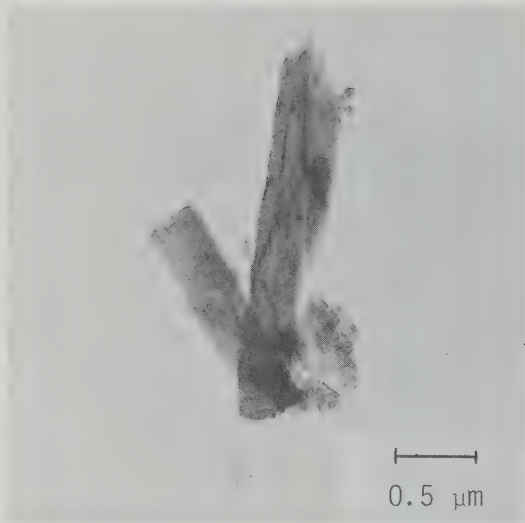
Figure 9. Transmission electron micrograph of chrysotile fibril after thermal degradation by electron beam irradiation.

Three modes of operation are possible in the TEM:

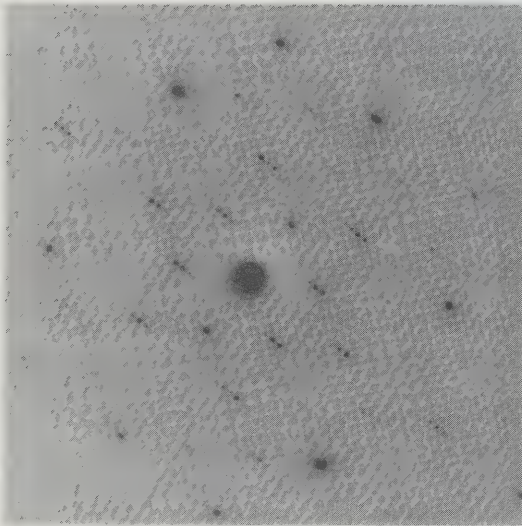
- a) in the imaging mode, electrons scattered from a point on the specimen are focussed at a single point in the image;
- b) in SAED operation, electrons scattered at a particular angle are focussed at a single point in the image plane. In a modern instrument, facilities are available for tilting and rotating the sample, so that the crystalline fibre may be examined along its principal crystallographic directions;
- c) electrons may be focussed to a point on the specimen, and an EDXA spectrum can be obtained from that point.

Switching between the different modes is accomplished simply by adjustment of lens currents and apertures. Examples of the three modes of operation are shown in Figures 10 and 11, which show results for antigorite and tremolite respectively.

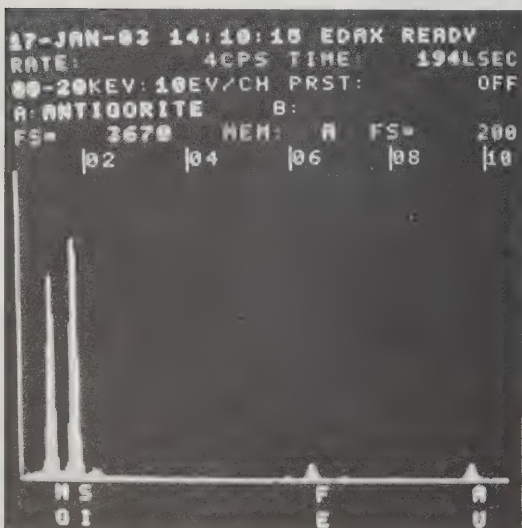
It is now generally agreed that transmission electron microscopy is the preferred instrumental technique for measurements of asbestos fibre concentrations in ambient atmospheres (73, 25, 47, 89, 99), since it incorporates the most powerful combination of identification methods. The modern instrument which includes SAED and EDXA capabilities is often referred to as the analytical electron microscope (AEM).



(a)



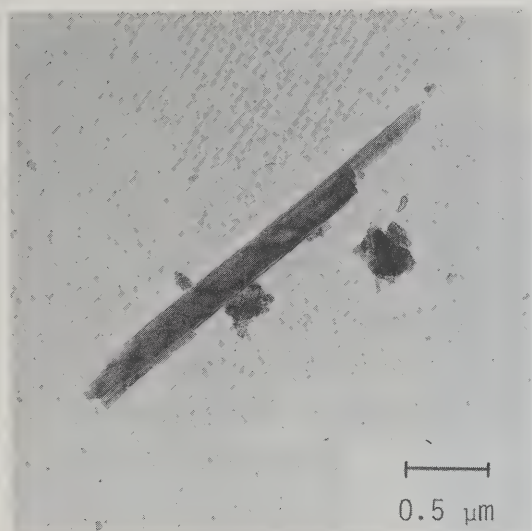
(b)



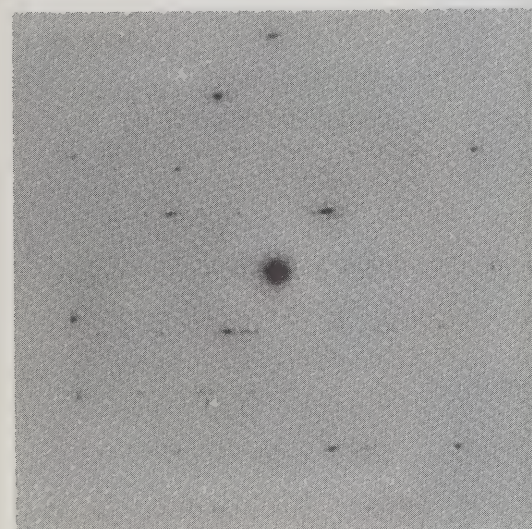
(c)

Figure 10. Example of the three modes of operation of a transmission electron microscope. Results shown for antigorite are:

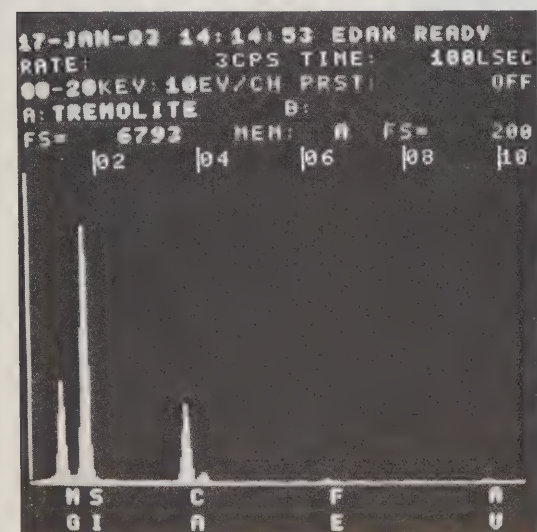
- (a) micrograph of particles
- (b) selected area electron diffraction (SAED) pattern;
- (c) energy dispersive X-ray (EDXA) spectrum.



(a)



(b)



(c)

Figure 11. Example of the three modes of operation of a transmission electron microscope. Results shown for tremolite are:

- (a) micrograph of particles;
- (b) selected area electron diffraction (SAED) pattern;
- (c) energy dispersive X-ray (EDXA) spectrum.

4. TEM ANALYTICAL PROCEDURES

4.1 Sample Collection and Preparation

Airborne dust samples for asbestos fibre counting can be collected using either of two different types of filter. The techniques used for preparation of TEM specimens from these filters require that the filter media should be completely removed before TEM examination. Two types of specimen preparation are possible: direct and indirect. The direct transfer procedure transfers particles from a particular area of the filter onto the same area of a TEM specimen. In the indirect methods, used particularly when concentration or dilution of the sample is required, the filter is ashed and the residual material is re-suspended in water. The water suspension can be prepared by a number of methods for TEM examination.

One type of filter used for sampling for airborne asbestos is the Nuclepore polycarbonate filter which is soluble in chloroform. Figure 12 shows the surface of this type of filter. The surface is relatively featureless apart from the cylindrical pores, and the particulate is collected on the surface. This type of filter is suitable for TEM specimen preparation by either the direct or the indirect procedure.

The other type of filter used in sampling for airborne asbestos is the conventional membrane filter, composed of esters of cellulose which are soluble in acetone. Figure 13 shows the surface of such a filter, and it can be seen that it is a depth type filter with a sponge-like structure. This filter has many advantages for sample collection. In particular, particles are retained efficiently during transportation to the analytical laboratory. The surface structure makes this type of filter unsuitable for preparation by direct transfer procedures. Accordingly, it is generally used only when indirect TEM specimen

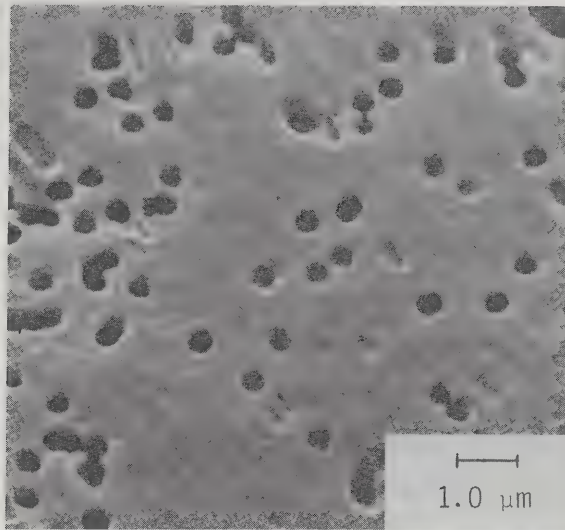


Figure 12. Scanning electron micrograph showing the surface of a 0.4 μm pore size Nuclepore polycarbonate membrane filter.

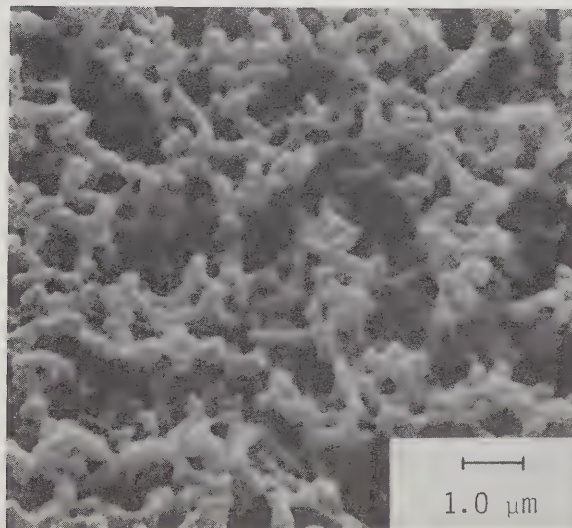


Figure 13. Scanning electron micrograph showing the surface of a 0.45 μm pore size conventional membrane filter.

preparation procedures are envisaged. However, some work is in progress to demonstrate that this type of filter is amenable to direct transfer procedures without incurring significant losses of fibres (70).

The volume of air to be drawn through the filter is ideally determined by the lowest fibre concentration which must be detected, and for a particular preparation technique it is possible to calculate the required air volume. However, the total suspended particulate concentration may be sufficiently high that this air volume would result in an undesirable degree of overlap of the particles collected on the filter surface and the samples would be unsuitable for direct preparation. If the specimen preparation technique to be used is a direct transfer method, care should be taken to ensure that the particulate deposit on the filter is uniform. Commercially-available filter assemblies often support Nuclepore filters in such a way that large areas of the filter are "blinded" by the porous support (27), and in these areas there will be no particulate deposit. The problem can be overcome by use of a coarse filter between the Nuclepore filter and the support (27). The properties of a particular filter holder should always be critically evaluated in this regard, since in the direct transfer preparation techniques the fibre count is based on only a small area of the filter.

If the preparation technique is to be an indirect one, the particulate loading of the filter is unimportant, provided that the analytical detection limit requirements can be met. Where samples are to be analyzed using an indirect preparation method and they cannot be hand-carried to the laboratory, the conventional membrane filter appears to be the best choice, and the filtration volume should be as high as practicable to minimize the effects of possible background contamination in the filter. Where samples can be carefully hand-carried to the laboratory, correctly-loaded Nuclepore filters can be analyzed by

the direct transfer preparation method.

4.2 Specimen Preparation Methods for the TEM

An essential feature of all preparation methods is that a representative and quantitative proportion of the sample should be mounted as a uniformly dispersed particulate deposit on the TEM specimen. For TEM specimens, the substrate on which the particles are mounted must be very thin so that it is transparent to 60 - 100 keV electrons. A suitable substrate is a continuous thin evaporated carbon film about 5 - 10 nm thick which is supported on a fine metal mesh. Particles supported on such a film can be examined in the open areas of the mesh.

Specimen preparation for the TEM has been a significant area of controversy. Of the methods that have been used, many have been discounted because of particle losses during preparation. In one study in which a variety of methods were used, inter-laboratory disagreement by a factor of 300 was reported (5). Some early methods depended on centrifugation (22), but these have largely been abandoned because they were susceptible to fibre loss and cross-contamination. Another group of methods, referred to as the "drop" methods, depended upon transfer of the particulate from the air filter to form a dispersion in water, a small volume of which was then micro-pipetted onto the carbon-coated TEM grids (46, 32). These methods were subject to the criticism that the particulate deposits on the TEM grid were not sufficiently uniform to allow a quantitative measurement to be made.

In a third group of methods, known as the direct transfer techniques, particulate deposits are transferred to the TEM grid by solvent dissolution of the membrane filter. The direct transfer techniques are now largely accepted as the most reliable methods for preparation of TEM specimen grids. There are a number

of variations of the direct transfer technique, but the carbon-coated Nuclepore procedure is now the most common approach.

The Nuclepore filter consists of a polycarbonate material which is soluble in chloroform. This type of filter is unique, in that it consists of a continuous, featureless plastic film, perforated by cylindrical holes of a narrowly defined size range. The surface structure of this filter presents no obstacles to the identification of particles on its surface. The steps in the carbon-coated preparation procedure are shown in Figure 14. After sample collection, the Nuclepore filter with particles on its surface is carbon-coated using a vacuum evaporator. Then, a small square of the coated filter is placed on a 200 mesh copper electron microscope grid, and the filter is dissolved away using chloroform in a simple reflux washer originally described by Jaffe (41).

Figure 15 shows the design of reflux washer used by Kalmus (43). This design has proved satisfactory in many fields of application. It consists of a supporting bridge made from a rectangular strip of stainless steel wire mesh bent sharply to form an inverted "U". The upper flat surface is covered lengthwise with a strip of paper lens tissue, slightly smaller in width than that of the bridge. Each end of the lens tissue strip is bent downwards so as to touch the floor of the petri dish in which the bridge is placed. Chloroform is added to a height just below the upper surface of the bridge in the petri dish. Grids are placed in the position illustrated, and a portion of the carbon-coated Nuclepore filter is placed on the top of each grid. The lid of the petri dish is then placed in position and the assembly allowed to stand for periods of up to two days, after which the plastic filter medium is completely dissolved, leaving a thin carbon film containing the embedded particulate.

It has been demonstrated that the carbon-coated Nuclepore

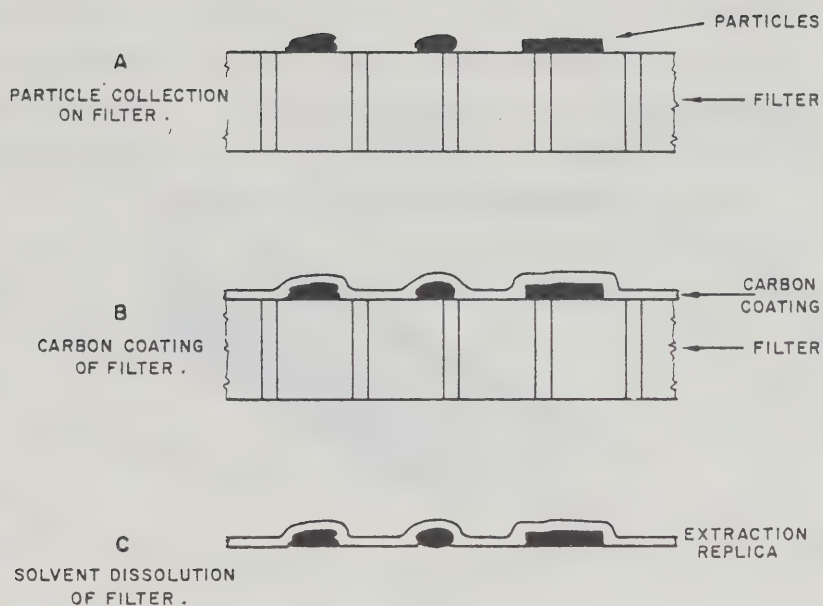


Figure 14. Steps in the carbon-coated Nuclepore procedure for TEM specimen preparation.

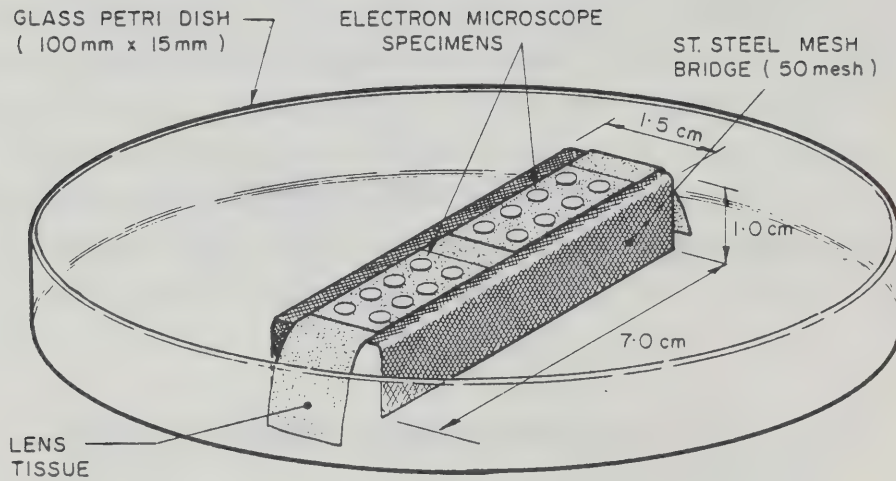


Figure 15. Design of Jaffe washer.

procedure can be performed without incurring losses of particles during the solvent extraction (27, 25). An analytical method for determination of asbestos in ambient air has been published by the U.S. Environmental Protection Agency (74), and this specifies the use of the Nuclepore filter.

Although preparation of Nuclepore filters for the microscope is simple and direct by the carbon-coating procedure, in practice the properties of this filter make it a most unsuitable medium for field use. In addition to the extreme difficulty of handling this delicate filter in the field, experience has been that particulate material becomes detached during transportation and handling. This loose material is either lost or at least moved to other parts of the filter surface. It is then impossible to sub-sample this filter in a representative manner. The direct preparation technique associated with the Nuclepore filter has no particular advantage if the filter is overloaded, as is often the case with environmental samples. The alternative is to sacrifice some of the analytical simplicity of the direct preparation in favour of a filter which is more satisfactory for field use. The structure of the conventional membrane filter retains the particulate in position during normal handling and transportation. Early analytical methods were based on the use of this type of filter.

In contrast to the Nuclepore filter, there is much surface detail associated with the conventional membrane filter and, if this detail is replicated by carbon evaporation, particles would be difficult to locate within it. Accordingly, most preparation methods have not incorporated carbon-coating of the filter surface. For the direct dissolution technique, a small square of the membrane filter is placed, deposit side down, onto a carbon-coated copper grid in a Jaffe washer, using acetone as the solvent. Beaman and File (12) considered that fibre losses associated with Jaffe washer preparations of the conventional

membrane filter were small and in general less than 10%. However, they used tetrahydrofuran as the solvent, but were unable to prepare samples suitable for particle identification. An alternative dissolution technique is based on the condensation washer, shown in Figure 16. This technique has been used by Beaman and File (12), McCrone and Stewart (51), and Millette and McFarren (54). Essentially, the device consists of a heated flask containing solvent, vapour from which is prevented from escaping by a vertical condenser. A side arm permits entry of a water-cooled cold finger, on which the membrane filter and carbon-coated grid assemblies are placed. Dissolution of the filter takes place over a period of some hours by a reflux washing action. The original purpose of this device was for the dissolution of plastic from carbon-coated plastic replicas, where loose particle movement is of no consequence. It has since been applied to the preparation of particulate samples with varying degrees of success. Opinions as to the proper operating conditions for the condensation washer vary, but there is agreement that fibre losses will at least be minimized if the washer is operated with the condensation level approximately at the position of the grids. Rapid operation will result in violent condensation action in the vicinity of the grids, and will inevitably result in fibre losses. A brass holder device, designed by Millette, permits easier handling of the carbon-coated grids and filter portions when assembling the washer.

It has been found that large and unreproducible particle losses occur when unfixed particles on conventional membrane filters are solvent-extracted. In a systematic study of specimen preparation methods, Chatfield et al (27) found mean fibre losses of up to 80% in groups of 10 samples when they were prepared from conventional membrane filters by solvent extraction, and the technique was reported to be strongly dependent on operator skill, if not totally unreproducible. Moreover, there was also evidence that the particulate deposits on the TEM specimens were

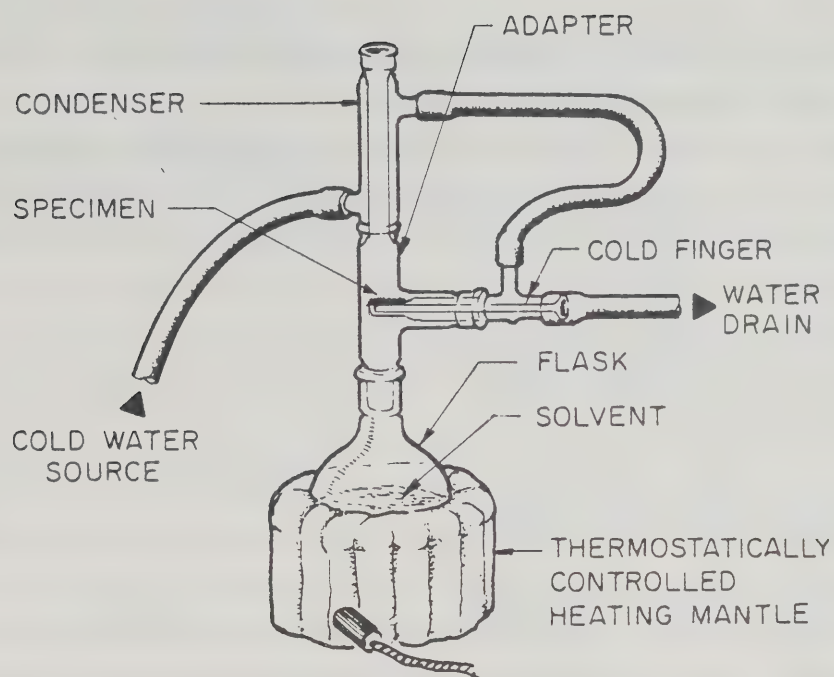


Figure 16. Condensation washer.

not uniform. In some cases only 10% of the specimens would pass a simple criterion for uniformity of the particulate deposits. In a review of various preparation methods available for the TEM, it was concluded that the carbon-coated Nuclepore procedure was the most satisfactory (27).

In view of the fact that the conventional membrane filter is probably the most convenient type for use in field sampling, there have been attempts to develop alternative direct transfer preparation techniques based on the use of this type of filter. A technique somewhat analogous to the Nuclepore procedure has been described by Ortiz and Isom (60). In this technique the sponge structure of the filter is collapsed into a continuous film by exposure to solvent vapour. The technique is excellent for preparing samples for the optical microscope, and has been in use for some years. Figure 17 shows the steps in TEM specimen preparation by this technique. After the filter structure has been collapsed, the surface is carbon-coated, and then the filter is dissolved by a Jaffe washer procedure using acetone as the solvent. This procedure yields a replica containing the particles which were originally on the surface of the filter. The technique requires that all of the fibres be retained on the surface of the filter after the collapsing process, so that they are available for entrapment in the evaporated carbon film; any particles that become covered during collapse of the structure will not be transferred to the TEM specimen. Obviously, particle losses using this method will be most serious at the larger pore sizes because during collection a greater proportion of the fibres will have penetrated deeply into the open framework structure of the filter. Some work has been performed (18) to assess the extent of fibre loss when TEM specimens are prepared by this method. Filters prepared using reference aqueous dispersions of both chrysotile and crocidolite were studied. In this work, it was found that the fibre losses increased with larger pore sizes and, for a particular pore size, the fibre losses increased as the fibre length decreased.



1. UNUSED MEMBRANE



2. AFTER FILTRATION



3. COLLAPSED MEMBRANE



4. CARBON COATED AFTER COLLAPSE



5. CARBON FILM AFTER DISSOLUTION

Figure 17. Steps in the collapsed membrane procedure for TEM specimen preparation.

For a pore size of 0.45 μm , significant losses of fibres longer than 5 μm occurred, and the fibre losses for larger pore sizes would appear to be unacceptably high.

A modification of the collapsed membrane technique has been examined in which, after the filter collapsing step, the filter is etched for a short time in a plasma asher (49). This procedure etches away a thin layer of the filter surface, and fibres which were engulfed during the collapsing step are brought to the surface again prior to carbon coating. This modification of the method should allow high transfer efficiencies to be obtained. However, only a few initial transfer efficiency measurements have been made (70), and these were not fibre-length-specific.

In order to achieve reliable identification and measurement, each particle must be clearly separated from adjacent particles on the TEM specimen. Therefore, when using a direct preparation technique, a suitably loaded sample filter is required. When there is a significant degree of overlap of the particles, and it is not desired or possible to re-sample, it is necessary in the preparation to reduce the concentration of the particulate on the final TEM specimen. This requires the use of an indirect specimen preparation technique, in which the particulate is removed from the filter into aqueous suspension, followed by filtration of an appropriate volume of the suspension. In the case of the Nuclepore filter, it has been found that the majority of the particulate can be removed from its surface into aqueous suspension by ultrasonic treatment. However, if the filter is ashed, it is possible to destroy specifically all of the organic particles. The ash is then dispersed in water using ultrasonic treatment, after which filters of appropriate particulate loading can be prepared by filtration of suitable volumes of the aqueous dispersion. In a technique first reported by Chatfield and Glass for analysis of water samples which have high concentrations of organic materials (26), the filter is ashed using a low

temperature plasma asher. After ashing, the residual material is re-dispersed ultrasonically in a small volume of double-distilled water. This suspension is then filtered through a 0.1 μm pore size Nuclepore filter, which is prepared for the electron microscope using the carbon-coating procedure discussed earlier. The validity of this preparation technique is, of course, contingent on a successful demonstration that the ultrasonic treatment used does not significantly change the fibre dimensions or concentrations reported.

In all of the preparation techniques discussed, contamination of the samples by extraneous fibres must be eliminated. It is recommended that all sample preparation be conducted in cleanroom facilities or in a laminar flow hood. Contamination of the samples by chrysotile is a significant problem, and this must be kept under continuous control by an extensive programme of blank measurements. Only when these blank measurements are insignificant compared with the levels being measured can the method be regarded as reliable. It is most important that all reagents and solutions must be filtered before use, preferably through a 0.1 μm pore size Nuclepore filter. Most reagents as purchased contain significant chrysotile fibre concentrations. The air sampling filters themselves may contain unacceptable levels of chrysotile fibre (17). Where the preparation technique includes ashing of the filters, particular attention should be given to blank measurements, since any asbestos contamination throughout the whole thickness of the original filter will appear on the final TEM specimen.

4.3 Fibre Identification Protocol

Precise methods for identification of asbestos fibres have never been specified as part of the published analytical procedures (74, 3). Consequently, the electron microscopist has been free to

decide what combination of measurements or observations constitutes an adequate identification for a particular fibre. Chrysotile was originally thought to be relatively simple to identify, since similar tubular morphology occurs in only a very few other minerals and its selected area electron diffraction (SAED) pattern has some characteristic features. However, it has been found that other species such as vermiculite can yield particles which have a scrolled structure, and these can be mistaken for chrysotile if the SAED patterns are not interpreted quantitatively (28). It has always been considered difficult to identify the precise mineral species of a single sub-micrometre fibre of amphibole. The layer type SAED patterns which are usually obtained have a 0.53 nm layer separation. Comparison of this type of pattern with those obtained from known amphibole asbestos fibres has often been accepted as identification for an amphibole fibre, but in fact many other minerals can yield similar or even identical patterns. Accordingly, the more cautious analyst has obtained EDXA spectra of at least a few of the fibres to provide additional confidence in the identification, although these analyses were not called for in the specified procedure. Even this approach is subject to error, since other minerals exist which have elemental compositions similar to those of the amphiboles. Therefore, as part of the analytical procedures for determination of asbestos fibre concentrations in air and water, a logical and practical protocol for fibre identification must be defined.

When the mineralogical species of the fibres has been correctly identified, the question still remains as to whether the fibres are actually asbestos. Although chrysotile presents little difficulty in this regard, it is not routinely possible in the TEM to classify an individual small amphibole fibre as either asbestos or as a non-asbestos cleavage fragment, since crystal habit is the only basis on which these can be discriminated. Previous work (97) has shown that populations of fibres which

originate from the fibrous and non-fibrous minerals can be discriminated on the basis of the distributions of their fibre aspect ratios. A demonstrated and reliable means of discrimination is necessary, since many minerals other than the asbestoses, but compositionally similar to them, yield fragments of relatively high aspect ratios.

4.3.1 General Considerations

Before it is incorporated into a fibre count, each particle with an aspect ratio of 3 to 1 or greater and not of obviously biological origin must be identified according to precisely defined criteria. Fibre internal morphology, chemical composition and crystal structure are the properties on which these criteria must be based.

Fibre internal morphology allows amphiboles and other crystalline mineral fibres to be discriminated from chrysotile and a few other minerals which display a tubular appearance in the TEM. Further analysis of each fibre must then be conducted using SAED and EDXA methods.

The crystal structure of some mineral fibres, such as chrysotile, is easily degraded by the high current densities required for EDXA examination. Therefore, SAED investigation of these sensitive fibres must be completed before attempts are made to obtain EDXA spectra. When examining more stable fibres, such as the amphiboles, the order of work is unimportant.

4.3.2 SAED Techniques

The SAED technique can be either qualitative or quantitative. For quantitative work, a thin film of gold

should be evaporated on the underside of the specimen grid as an internal calibration of camera length. Qualitative SAED consists of visual examination of the pattern obtained on the microscope screen from a randomly oriented fibre. SAED patterns obtained from fibres with cylindrical symmetry, such as chrysotile, are an exception since they are not sensitive to axial tilt, and patterns from randomly oriented fibres can be interpreted quantitatively. For non-cylindrical fibres, quantitative (zone axis) SAED requires alignment of the fibre so that a principal crystallographic axis is parallel to the electron beam. The pattern is then recorded and its consistency with zone axis patterns from known mineral structures can be examined. The SAED pattern obtained from one zone axis may not be sufficiently specific to identify the mineral fibre, but it is often possible to tilt the fibre to another angle and to record a different zone axis pattern. The angle between the two axes can also be checked for consistency with the structure of a suspected mineral.

For visual examination of the SAED pattern, the camera length of the TEM should be set to a low value and the SAED pattern then should be viewed through the binoculars. This procedure minimizes the irradiation and possible degradation of the fibre. However, the pattern is distorted by the tilt angle of the viewing screen. For recording purposes, a camera length of about 2 metres must be used if accurate measurement of the pattern is to be possible. It is of extreme importance that, when obtaining an SAED pattern for either recording or visual evaluation, the sample height should be properly adjusted to the eucentric point and the image should be focused in the plane of the selected area aperture. If this is not done there may be some components of the SAED pattern which do not originate from the selected area. It will be found in general that the smallest SAED

aperture will be necessary.

If a zone axis SAED analysis is to be attempted on the fibre, the sample must be in the appropriate holder. The most convenient holder allows complete rotation of the sample and single axis tilting. The sample should be rotated until the fibre image indicates that the fibre is oriented with its length coincident with the tilt axis of the goniometer. The sample height should then be adjusted until the fibre is at the eucentric position. The fibre is tilted until a pattern appears which is a symmetrical, two dimensional array of spots. The recognition of zone axis alignment conditions requires some experience on the part of the operator. Not all zone axis patterns which can be obtained are useful or definitive. Only those which have closely-spaced reflections corresponding to low indices in at least one direction should be recorded. Patterns in which all d-spacings are less than about 0.3 nm are not useful and are usually very wasteful in computer analysis time. A useful guideline is that the lowest angle reflections should be within the radius of the first gold diffraction ring (111), and that patterns with smaller distances between the reflections are usually the most definitive.

4.3.3 EDXA Techniques

Correct identification of individual mineral fibres requires quantitative data on their compositions. In addition, the quantitative analysis procedure should be transferrable between instruments.

The technique described by Cliff and Lorimer (30) offers a convenient method by which relatively accurate (~10%) quantitative analyses can be obtained. The X-rays generated

in a thin specimen by an incident electron beam have a low probability of interacting with the specimen. Thus the mass absorption and fluorescence effects are negligible. In a specimen composed of elements I and J, the following relationship can be used to perform quantitative analyses in the TEM:

$$\frac{A_I}{A_J} = k \frac{C_I}{C_J}$$

where A_I and A_J are the measured elemental integrated peak areas, C_I and C_J are the weight or atomic fractions of the two elements, and k is a constant. To incorporate correction for the particle size effect on peak area ratios (83), the Cliff and Lorimer technique has been extended by obtaining separate values of k for different ranges of fibre diameter.

Calibration of the TEM-EDXA combination is achieved using reference silicate minerals. Great care must be exercised in selection of suitable calibration standards, so that they are as homogeneous as possible. Since many of the fibre analyses will involve the commercial asbestos varieties, some of the standards should be selected to have compositions close to these. The calibration is performed by comparing microprobe analyses of polished sections of the mineral standards with EDXA spectra from the same mineral in the TEM.

The quantitative EDXA technique can readily be transferred to another system with only a minimum of calibration. Standards of some selected minerals have been prepared on TEM grids for this purpose, and the only requirement is to obtain EDXA spectra from about 20 particles of each mineral.

4.3.4 Optimum Fibre Identification Procedure

Usually, the most expedient method for fibre identification is to select on the basis of chemical composition those minerals consistent with the EDXA spectrum of the unknown fibre. The more labour-intensive technique of quantitative interpretation of zone axis SAED patterns can then be used for comparison with a limited number of possible minerals, rather than with the entire mineral vocabulary.

4.3.5 Instrumental Limitations

Modern analytical electron microscopes (AEM) have resolutions of the order of 0.2 nm, which is adequate for imaging of the smallest fibres of interest. However, in using the instrument an appreciation of the analytical limitations is required.

The smallest area of the image from which an SAED pattern can be obtained is obviously a critical factor in the analyses, since it may be impossible in a heavily-loaded specimen to completely isolate a particular fibre under investigation. The smallest area which can be analyzed without interference from surrounding particles is given by:

$$A = \frac{\pi}{4} \left(\frac{D}{M} + 2000 C_s \theta^3 \right)^2$$

where:

A = Effective SAED area in μm^2

D = Diameter of SAED aperture in μm

M = Magnification of objective lens

C_s = Objective lens spherical aberration coefficient
in mm

θ = Maximum required Bragg angle in radians

For Bragg angles less than 0.01 radians the instrument must be capable of performing selected area electron diffraction from an area of $0.6 \mu\text{m}^2$ or less, selected from an in-focus image at a screen magnification of 20,000. This performance requirement defines the minimum separation between particles at which independent diffraction patterns can be obtained from each. Although almost all instruments of current manufacture meet these requirements, many older instruments which are still in service do not. It is obviously not possible to reduce the area of analysis indefinitely by use of apertures smaller in diameter than those specified by the manufacturer, since there is a fundamental limitation imposed by the spherical aberration coefficient of the objective lens. It is extremely important that before SAED operation is attempted, the image should be properly focussed, since the analyzed area expands rapidly with the degree of de-focus.

For EDXA measurements, the AEM should have an illumination and condenser lens system which is capable of forming electron probes 100 nm or less in diameter. The minimum probe diameter possible is limited by the spherical aberration of the condenser lens system, and in some instruments the minimum beam diameter may not have adequate current density for the X-rays generated from very thin fibres to be detected. In some instruments, this problem is overcome by performing all EDXA measurements in scanning transmission electron microscopy mode (STEM).

It is not always possible to collect SAED and EDXA data from a particular fibre. It may not be possible to obtain a satisfactory SAED pattern if the fibre is too close to a bar of the support grid. When the sample is tilted to locate a zone axis, the grid bar may then obscure the fibre. The fibre may also be inappropriately tilted about an axis

perpendicular to the goniometer tilt axis so that no principal zone axes are encountered within the range of the goniometer. A double-tilt goniometer allows precise alignment of a fibre zone axis, but in this type of goniometer it is not possible to align the fibre axis with one of the tilt axes. If the fibre is large, extensive twinning in the structure may prevent the observation of a simple zone axis pattern. In the case of EDXA, the fibre may be too close to a bar of the support grid, giving rise to a high background signal unrelated to that from the fibre. In other cases, the grid bars or particulate on the sample may shield the detector and no spectrum from the fibre will be obtained.

4.3.6 Fibre Classification Categories

It is not always possible to proceed to a definitive identification of a fibre; this may be due to instrumental limitations, obstruction by sample support grid bars or the actual nature of the fibre. In many analyses a definitive identification of each fibre may not actually be necessary if there is other knowledge available about the sample, or if the concentration is below a level of interest. The analytical procedure must therefore take account of both instrumental limitations and varied analytical requirements. Accordingly, a system of fibre classification has been devised to permit accurate recording of data.

In this identification protocol the general principle is to establish the most specific fibre classification (target classification) which is to be attempted, and then to record for each fibre the classification which is actually achieved. Depending on the intended use of the results, criteria for acceptance of fibres as "identified" can then

be established at any time after completion of the analysis.

The classifications as shown in Tables 1 and 2 are directed towards identification of chrysotile and amphibole fibres respectively. In an unknown sample, chrysotile can be regarded as confirmed only if a recorded, calibrated SAED pattern from a representative fibre in the CD category is obtained. Amphibole can be regarded as confirmed only by obtaining recorded data which yields exclusively amphibole solutions for fibres classified in the AZQ, AZZ or AZZQ categories.

4.3.7 Classification of Fibres With Tubular Morphology, Suspected to be Chrysotile

Many fibres are encountered which have tubular morphology similar to that of chrysotile, but which defy further attempts at characterization by either SAED or EDXA. They may be non-crystalline, in which case SAED techniques are not useful, or they may be in a position on the grid which does not permit an EDXA spectrum to be obtained. Alternatively, the fibre may be of organic origin, but not sufficiently definitive that it can be disregarded. Classification attempts for individual fibres of the same mineral will meet with various degrees of success. Figure 18 shows the classification procedure used for fibres which display any tubular morphology. The chart is self-explanatory, and essentially every fibre is eventually rejected as a non-asbestos mineral (NAM), or classified in some way which could still contribute to the chrysotile fibre count.

Morphology is the first consideration, and if this is not similar to that usually seen in chrysotile standard samples,

TABLE 1

CLASSIFICATION OF FIBRES WITH TUBULAR MORPHOLOGY

TM	-	Tubular Morphology not sufficiently characteristic for classification as chrysotile
CM	-	Characteristic Chrysotile Morphology
CD	-	Chrysotile SAED pattern
CQ	-	Chrysotile composition by Quantitative EDXA
CMQ	-	Chrysotile Morphology and composition by Quantitative EDXA
CDQ	-	Chrysotile SAED pattern and composition by Quantitative EDXA
NAM	-	Non-Asbestos Mineral

TABLE 2

CLASSIFICATION OF FIBRES WITHOUT TUBULAR MORPHOLOGY

UF	-	Unidentified Fibre
AD	-	Amphibole by random orientation SAED (shows layer pattern of 0.53 nm spacing)
AX	-	Amphibole by qualitative EDXA. Spectrum has elemental components consistent with amphibole
ADX	-	Amphibole by random orientation SAED and qualitative EDXA
AQ	-	Amphibole by Quantitative EDXA
AZ	-	Amphibole by one Zone Axis SAED
ADQ	-	Amphibole by random orientation SAED and Quantitative EDXA
AZQ	-	Amphibole by one Zone Axis SAED pattern and Quantitative EDXA
AZZ	-	Amphibole by two Zone Axis SAED patterns with consistent inter-axial angle
AZZQ	-	Amphibole by two Zone Axis SAED patterns, consistent inter-axial angle and Quantitative EDXA
NAM	-	Non-Asbestos Mineral

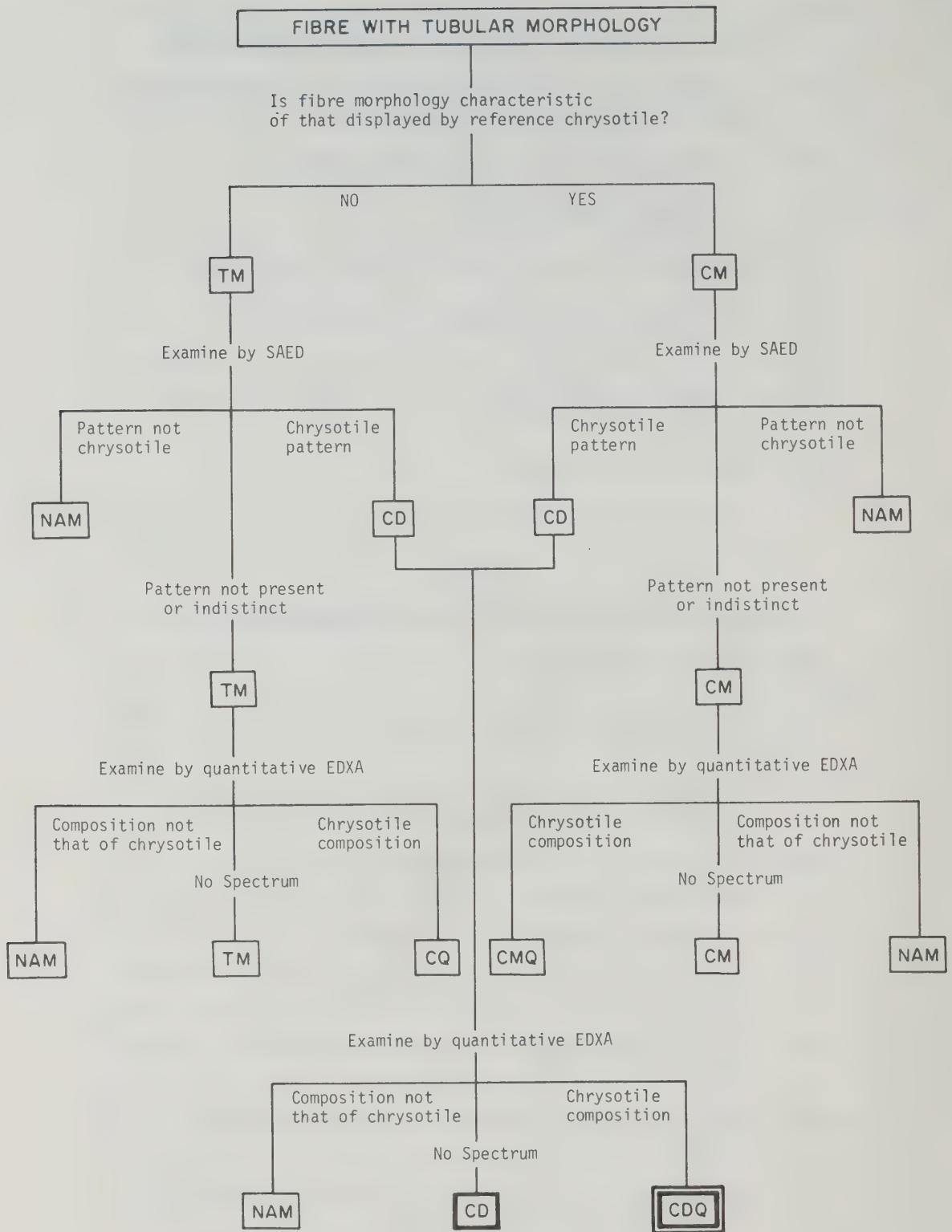


Figure 18. Classification chart for fibre with tubular morphology.

the initial classification is TM. Regardless of the doubtful morphology, the fibre is still examined by SAED and EDXA methods according to Figure 18. It may be possible to classify the fibre as having chrysotile morphology (CM) if it possesses the following morphological characteristics:

- a) the individual fibrils should have high aspect ratios exceeding 10:1 and they should be about 40 nm in diameter;
- b) the electron scattering power of the fibre at 60 to 100 kV accelerating potential should be sufficiently low for internal structure to be visible; and
- c) there should be some evidence of internal structure suggesting a tubular appearance similar to that shown in Figure 8, which may degrade in the electron beam to the appearance shown in Figure 9.

Every fibre having these morphological characteristics is examined by the SAED technique, and only those which give diffraction patterns with the precise characteristics of Figure 19 should be classified as chrysotile by SAED (CD). The relevant features in this pattern for identification of chrysotile are indicated in Figure 19. The (002) reflections should be examined to determine that they correspond approximately to a spacing of 0.73 nm, and the layer line repeat distance should correspond to 0.53 nm. There should also be "streaking" of the (110) and (130) reflections. Using millimetre calibrations on the microscope viewing screen, these observations can readily be made at the instrument. A TEM micrograph of at least one representative fibre should be recorded, and its SAED pattern should also

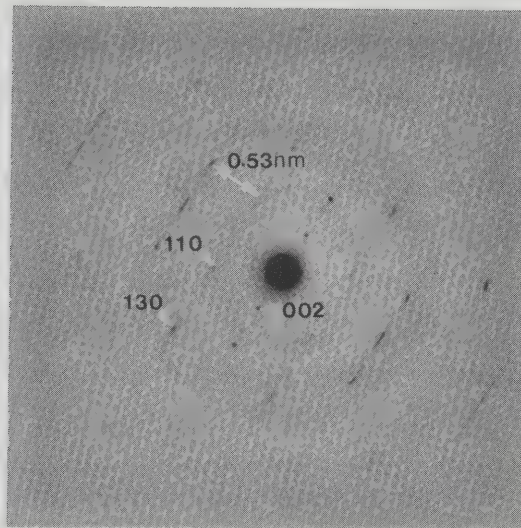


Figure 19. SAED pattern of chrysotile fibre with diagnostic features labelled. Necessary criteria are the presence of 0.73 nm spacing for the 002 reflections, 0.53 nm spacing for the layer line repeat, and characteristic streaking of the 110 and 130 reflections.

be recorded on a separate film or plate. This plate must carry calibration rings from a known polycrystalline substance such as gold. This calibrated pattern is the only documentary proof that the particular fibre is chrysotile and not some other tubular or scrolled species such as halloysite, palygorskite, talc or vermiculite.

The proportion of fibres which can be successfully identified as chrysotile by SAED is variable, and to some extent dependent on both the instrument and the procedures of the operator. The fibres that fail to yield identifiable SAED patterns will remain in the TM or CM categories unless they are examined by EDXA.

In the EDXA analysis of chrysotile, there are only two elements which are relevant. For fibre classification, the EDXA analysis should be quantitative. If the spectrum displays prominent peaks from magnesium and silicon, with their areas in the appropriate ratio, and with only minor peaks from other elements, the fibre should be classified as chrysotile by quantitative EDXA, in the categories CQ, CMQ or CDQ, as appropriate.

For chrysotile analyses there are essentially three possible levels of analysis:

1. morphological and SAED discrimination only (target classification CD);
2. in addition, EDXA of only those fibres which remained unclassified by SAED (target classification CD);
3. EDXA in addition to SAED of all fibres (target classification CDQ).

4.3.8 Classification of Fibres Without Tubular Morphology, Suspected to be Amphibole

Every particle without tubular morphology and which is not obviously of biological origin, with an aspect ratio of 3 to 1 or greater and having parallel or stepped sides, should be considered as a suspected amphibole fibre. Further examination of the fibre by SAED and EDXA techniques will meet with a variable degree of success, depending on the nature of the fibre and on a number of instrumental limitations. It will not be possible to identify every fibre completely, even if time and cost are of no concern. Moreover, confirmation of the presence of amphibole can be achieved only by quantitative interpretation of zone axis SAED patterns (48), a very time-consuming procedure. For routine samples from unknown sources, zone axis SAED work should be performed on at least one fibre typical of each compositional class reported. When a higher degree of certainty is required, it may be necessary to identify more fibres by the zone axis technique. When analyzing samples from well-characterized sources, the cost of identification by zone axis methods may not be justified.

The 0.53 nm layer spacing of the random orientation SAED pattern is not by itself diagnostic for amphibole. However, the presence of c-axis twinning in many fibres leads to contributions to the layers in the patterns by several individual parallel crystals of different axial orientations. This apparently random positioning of the spots along the layer lines, as shown in Figure 20, if also associated with a high fibre aspect ratio, is a characteristic of some types of amphibole asbestos, and thus has some limited diagnostic value. If a pattern of this type is not obtained, the identity of the fibre is still ambiguous, since the absence of a recognizable pattern may

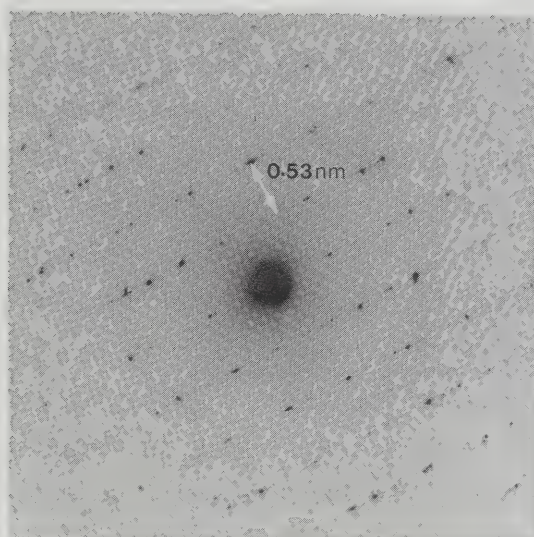


Figure 20. Amphibole SAED pattern (crocidolite) obtained from a fibre without precise orientation onto a zone axis.

be a consequence of an unsuitable orientation relative to the electron beam, or the fibre may be of some other mineral species.

As for chrysotile, the procedure is first to define the target level of classification to be attempted, and then to record the degree of success achieved for each fibre. The fibre classification chart for suspected amphibole fibres is shown in Figure 21. This chart shows all the classification paths possible in the analysis of a suspected amphibole fibre, when examined systematically by SAED and EDXA. Initially two routes are possible, depending on whether an attempt to obtain an EDXA spectrum or a random orientation SAED pattern is made first. The normal procedure for analysis of a sample of unknown origin is to examine the fibre by random orientation SAED, qualitative EDXA, quantitative EDXA, and Zone Axis SAED in this sequence. The final fibre classification assigned will be defined either by successful analysis at the target level or by the instrumental limitations. The maximum classification achieved for each fibre is recorded. The various classification categories can then be combined later in any desired way for calculation of the fibre concentration, and a complete record of the results from each fibre is maintained for re-assessment of the data if necessary.

Depending on the particular situation, four levels of analysis for suspected amphibole can be defined in this analytical procedure, and these are shown in Table 3.

In the routine unknown sample, a level 3 analysis is required if the presence of amphibole is to be confirmed. For this level of analysis, attempts are made to raise the classification of every fibre to the ADQ category. In addition, at least one fibre from each type of suspected

TABLE 3
LEVELS OF ANALYSIS FOR AMPHIBOLE

Level of Analysis	Application	Target Classification for all Fibres	Required Classification for Confirmation of Amphibole in a Proportion of the Fibres
1	Routine monitoring of known and well-characterized sources for one mineral fibre type.	ADX	Not Applicable
2	Routine monitoring of known and well-characterized sources where discrimination between two or more amphibole fibre types is required.	ADQ	Not Applicable
3	Routine samples from uncharacterized sources in which presence or absence of amphibole is to be confirmed.	ADQ	AZZ, AZQ or AZZQ - Solutions must include only amphiboles.
4	Samples where precise identification of all amphibole fibres is an important issue.	AZQ	AZZQ - Solutions must include only amphiboles.

amphibole found must be examined by zone axis SAED methods to confirm the identification.

4.3.9 Analysis of Fibre Identification Data

Because the fibre identification procedure is involved and time-consuming, a Fortran computer programme has been developed which permits the work to be performed by individuals without extensive training in mineralogy. This programme permits the EDXA and zone axis SAED measurements to be compared against a library of compositional and structural data for 226 minerals. The mineral library includes fibrous species which have been listed by several authors, together with other minerals which are known to be similar to amphibole or chrysotile in either their compositions or some aspects of their crystallography. Amphibole compositional ranges and terminology were adopted in accordance with the most recent mineralogical classification (38). An example of a single mineral entry in the file is shown in Table 4. The nominal composition for the mineral is stated, along with the permitted ranges of the number of atoms for four mandatory elements. In the case of cummingtonite, the published ranges for the mandatory elements are Si (8.00), Mg (2.10 - 4.90), and Fe (2.10 - 4.90). Elements which may also be present, but are not mandatory in this mineral, are Ca (0 - 1.34), Na (0 - 1.34). The crystallographic data are also listed together with a numerical code for the symmetry group.

Additional minerals may be added to the library if they are thought to be of concern in particular situations. The addition of new minerals to the data file does not require any further calibration of the EDXA system.

TABLE 4

AN EXAMPLE OF A SINGLE MINERAL ENTRY
IN THE LIBRARY MINERAL FILE

NAME : CUMMINGTONITE
FORMULA : (FE,MG)7 SI8 O22 (OH)2
MANDATORY : 14 8.00 8.00 12 2.10 4.90 26 2.10 4.90 0 0.00 0.00
OPTIONAL : 20 0.00 1.34 11 0.00 1.34 0 0.00 0.00 0 0.00 0.00
A,B,C,ALPHA,BETA,GAMMA,SYM: 9.600 18.300 5.300 90.000101.833 90.000 5

It is important to recognize that consistency of compositional data from an unknown fibre with the data for a particular comparison mineral does not uniquely identify the unknown, since the possibility exists that data from other minerals may also be consistent. It is, however, very unlikely that a mineral of another structural class could yield data consistent with that from an amphibole fibre identified uniquely by the AZZQ procedure.

The computer programme classifies fibres initially on the basis of chemical composition. Either qualitative or quantitative EDXA information may be used. The procedure using qualitative EDXA consists of entering the list of elements which originate from the particle. For quantitative EDXA, the list of elements and the areas under the corresponding X-ray emission peaks, after background correction, are the input data for the computer programme. The calculated elemental composition of the unknown is then compared with each mineral in the stored mineral library. The programme selects from the file a list of minerals which are consistent in composition with that measured for the unknown fibre. The published compositional ranges specified in the data file are increased by $\pm 20\%$ to accommodate experimental error. For a mineral to be selected as consistent in composition, the mandatory elements must be present in the unknown, and, if the input data are quantitative, then the mandatory elements must be present within these bounds. In addition, the remaining elements entered for the unknown fibre are compared either qualitatively or quantitatively with the optional elements in the comparison mineral. A maximum of two discrepancies are allowed for the optional element comparison. Table 5 shows an example of the output obtained for a fibre of riebeckite. It can be seen that the original list of 226 minerals has been reduced to three compositionally-consistent varieties.

TABLE 5

OUTPUT FROM A COMPUTER ANALYSIS OF QUANTITATIVE EDXA SPECTRUM
FROM A FIBRE OF RIEBECKITE

PARTICLE IDENTIFICATION

PARTICLE: RIEBECKITE

WIDTH OF PARTICLE: 1.200 micrometers

X-RAY SPECTRUM:	ELEMENT	PEAK AREA	ELEMENT	PEAK AREA
	SI	1000.00	FE	436.00
	NA	98.00		

CALCULATED ATOMIC RATIOS:	ELEMENT	RATIO	ELEMENT	RATIO
	SI	1.000	FE	0.402
	NA	0.398		

MINERALS WITH COMPOSITIONS CONSISTENT WITH X-RAY SPECTRUM

CROSSITE	NA2 (MG,FE)3 (FE,AL)2 SI8 O22 (OH)2
FE-RICHTERITE	NA CA NA FE5 SI8 O22 (OH)2
RIEBECKITE	NA2 FE3 FE2 SI8 O22 (OH)2

The programme is linked to an electron diffraction pattern analysis routine which is an extension of that originally developed by Rhoades (69). This version of the programme requires measurements of 5 reflections from the zone axis SAED pattern, which are then tested for consistency with the crystallographic data of the minerals previously selected as compositionally-consistent with the unknown fibre. If more than a single mineral are still reported, measurements from an additional zone axis SAED pattern can be entered, together with the tilt angle observed between the positions at which the two patterns were obtained. Two zone axis patterns for the riebeckite example are shown in Figures 22 and 23, and in this case it was not possible from these data to discriminate between richterite and riebeckite, both of which are amphiboles.

4.3.10 Reporting of Fibre Classifications

Before the fibre count data can be processed to give concentration values, a decision must be made as to which fibre classifications are to be considered adequate as identification of the fibre species in question. This decision will depend on how much is known about the particular source from which the sample was collected.

If the sample is from a completely uncharacterized source, it is recommended that the classified fibres be grouped as below:

- a) Confirmed Amphibole: AZZQ + AZQ + AZZ
(Solutions must include only amphiboles)

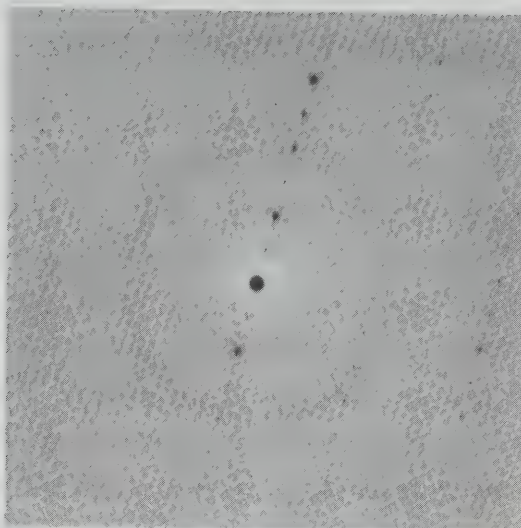


Figure 22. Zone axis SAED pattern from riebeckite, including ring diffraction pattern from gold used as calibration of microscope camera length.

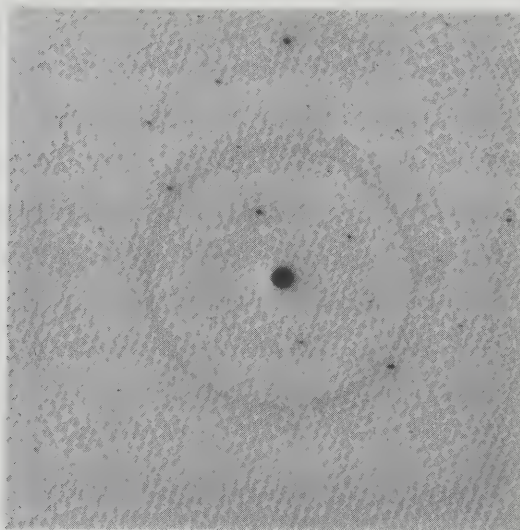


Figure 23. Zone axis SAED pattern from riebeckite, including ring diffraction pattern from gold used as calibration of microscope camera length.

- b) Amphibole Best Estimate: $AZZQ + AZQ + AZZ + AZ + ADQ + AQ$
- c) Suspected Amphibole: $ADX + AX + AD$
- d) Confirmed Chrysotile: $CDQ + CD$
- e) Chrysotile Best Estimate: $CDQ + CD + CMQ + CQ$
- f) Suspected Chrysotile: CM

The Best Estimate should be reported only if some fibres are also reported in the confirmed category, otherwise all fibre classifications must be reported as suspected amphibole or suspected chrysotile.

4.4 Fibre Counting

The TEM specimen consists of a 3 mm diameter copper mesh, on which the thin carbon film containing the embedded particles and fibres is supported. The mesh openings are about 85 μm square. It is good practice to prepare grids from several positions on the air sample filter, since the fibre count is made on a very small area (less than 0.2 mm^2) of the filter. If the results from such grids are statistically compatible, it indicates that the particulate deposit is reasonably uniform over the whole filter, and that the grids will yield a representative fibre count. The procedure is to count all fibres on a total of about 20 grid openings. Before it is incorporated into the fibre count, each fibre is identified, and its dimensions are recorded by comparison with calibration marks on the TEM screen. The numbers of fibres found on each grid opening are recorded separately, since this information allows a calculation of the precision to be made.

If the distribution of fibres on the sample is shown to pass a chi-squared uniformity criterion, there is no reason to discard the hypothesis that the fibres are distributed according to a Poisson distribution. In this case the 95% confidence interval can be obtained from published tables (62). Where the deposit can be shown not to be distributed according to a Poisson distribution and adequate numbers of fibres have been counted, the 95% confidence interval must be calculated using the fibre counts obtained on the individual grid openings. This is performed using Gaussian statistics, and for this purpose the fibre count should include a minimum of 4 grid openings.

The fibre counting criteria are still a matter of some controversy. There are varying opinions as to how fibre bundles with split ends, fibre aggregates, and fibres attached to non-fibrous debris should be treated. The analyst must at least be consistent, and the procedure should define carefully the actions to be taken. A particularly difficult problem is posed by fibrous aggregates which are of marginally respirable dimensions. Figure 24 shows a TEM micrograph of an aggregate of material collected in an area of Maryland where the unpaved roads were covered with serpentine rock containing chrysotile. It is difficult to say how many fibres this feature represents, and this uncertainty is of concern since many of these particles have dimensions in the respirable size range. If the SEM is used to examine a particle of this type, it can be seen that there are many more aggregated fibres which are not visible in the TEM image. An SEM micrograph of a typical particle is shown in Figure 25. There are reasons to think that the indirect specimen preparation methods involving aqueous re-dispersal of the particulate alleviates these problems of fibre counting, although there has as yet been very little research into the comparison of the direct and indirect preparation methods.

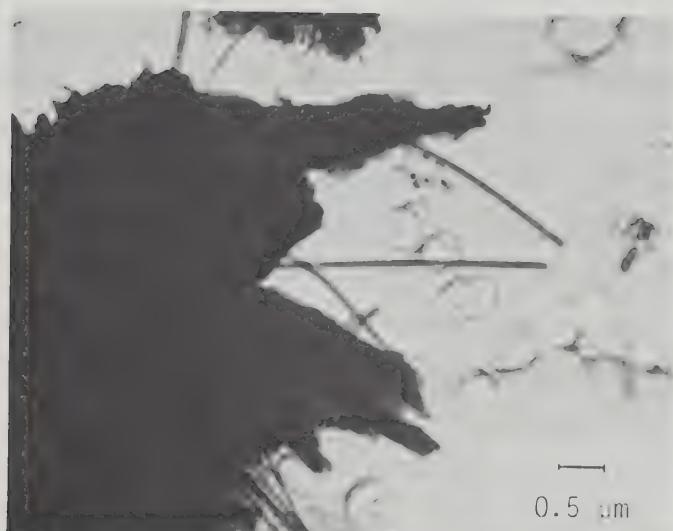


Figure 24. Transmission electron micrograph of an aggregate of material found in an ambient air sample.

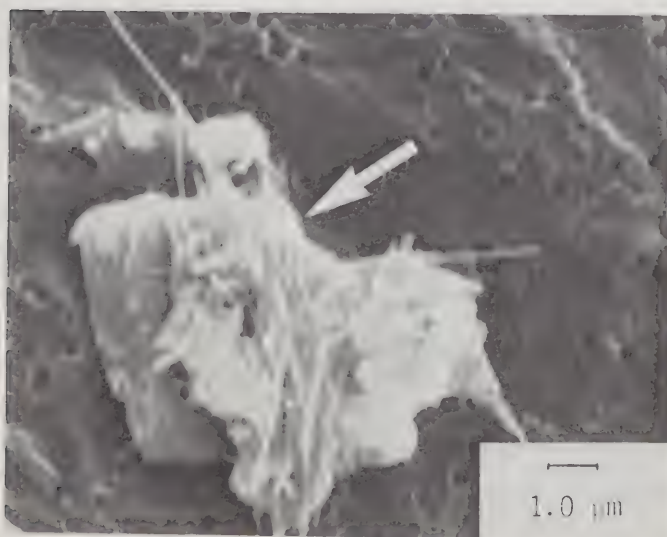


Figure 25. Scanning electron micrograph of an aggregate of material found in an ambient air sample. Many fibres can be seen which would not be observed during routine TEM examination.

4.5 Reporting of Results

The calculation of the results is rather trivial; but in view of the large amount of data collected for each sample, it is convenient to use a computer. The fibre counting technique has progressed significantly since the time when a simple concentration value was reported without any information on precision. A suitable format for data reporting has been developed (24), and this forms the basis of the procedure under consideration by a working group of the International Organization for Standardization (ISO). The quantities to be reported are summarized below:

- a) A test for uniformity of the fibre deposit on the samples should be conducted using the chi-squared test. Samples which do not pass this test should be re-prepared.
- b) The mean and the 95% confidence interval of the fibre concentration should be reported, along with a statement of whether Poissonian or Gaussian statistics have been used. Where the result is on the basis of fewer than 5 fibres, no mean value should be reported. In this case the upper 95% confidence limit (Poisson) should be quoted as the detection limit.
- c) The mass concentration should be calculated by summation of the volumes of the fibres and assumption of a value for the density.
- d) Fibre length, width, mass and aspect ratio distributions should be calculated.
- e) For each fibre type reported, proof of fibre identification should be obtained if the analyses are to be the subject of legal challenges.

- f) The analytical sensitivity, i.e. the fibre concentration which corresponds to one fibre detected, should always be stated.

5. AMBIENT ASBESTOS FIBRE MEASUREMENTS

There is not a large amount of literature on the topic of ambient asbestos fibre concentrations. Unfortunately, different analytical methods have been used for the various studies which have been conducted, and this aspect alone makes comparison of the results rather difficult. Some of the earlier studies may also have been seriously affected by asbestos contamination of the membrane filters used for air sampling. Chatfield reported the existence of such contamination (17) which, because of its variability from filter to filter, cannot be considered as a constant background to be subtracted from air sample measurements. In essence, it can be stated that measurement of low concentrations of airborne asbestos fibres requires considerable skill, even when using the latest techniques, and that the results of work performed before about 1976 should be viewed with considerable caution. Even as late as 1977, in parallel analyses conducted by several laboratories on divided filters, it was stated that the variability of the measured asbestos fibre concentrations was so large that no conclusions could be drawn from the data (6). However, the analytical procedures used by the different laboratories were very different, and some were even designed to deliberately break up the fibres so that mass concentration measurements could be made more accurately. It is not surprising, therefore, that inconsistent results were obtained.

Although in some studies a constant relationship has been assumed between fibre number and fibre mass concentrations (14, 34), this is in general an unwarranted assumption because the actual relationship varies and depends on the fibre size distribution. The only reliable conversion is to compute the mass concentration from the number of fibres and their dimensions. Moreover, the value of the mass concentration is particularly sensitive to the inclusion of statistically infrequent large fibres, and a completely different fibre counting strategy should be employed if mass concentration is the primary interest. This strategy is directed towards obtaining

statistically-valid fibre counts for the large fibres which contribute most to the mass measurement. In contrast, the usual fibre counting strategy for determination of numerical fibre concentrations gives most reliable information on the smaller fibres, but this strategy has frequently been used for determination of mass concentrations. Where results are quoted in terms of both numerical and mass concentrations, the method of conversion should be specified. The relevance of mass concentration measurements to the estimation of risk from exposure is discussed later.

Recently, possible exposures of the general population to airborne asbestos fibres originating from construction materials or other products have given rise to some concern, and in this context two situations have been considered: the atmospheres in buildings and in subway transit systems. Asbestos-containing insulation materials are commonly used on the interior structures of buildings; and it is considered possible for fibres from these materials to become airborne and then distributed throughout the building by the air handling systems. It has also been suggested that erosion of vinyl-asbestos floor tile in normal use may also contribute to elevated airborne fibre concentrations (79). In subway transit systems, acoustic insulation in the tunnels often contains asbestos, and it is thought possible that this may release airborne fibres. The trains themselves use brake linings which incorporate asbestos, and particulate material from these is dispersed during each application of the brakes.

5.1 Asbestos Fibre Concentrations in Ambient Atmospheres

There have been only a few systematic studies of asbestos fibre concentrations in the general environment. In some early work it was concluded that the chrysotile level in urban atmospheres may be about 0.1 ng/m^3 (68). Selikoff et al (82) found $10 - 60 \text{ ng/m}^3$ in New York City and 100 ng/m^3 in some locations. Sebastien et al (76) have reported that airborne asbestos fibre concentrations

in Paris range between the detection level of 0.1 ng/m^3 and 10 ng/m^3 . Nicholson et al (58) reported the distribution of chrysotile concentrations in the ambient air of U.S. cities, and these ranged from 1 ng/m^3 to 100 ng/m^3 .

It should be recognized that in the work of both Selikoff et al and Nicholson et al an analytical technique was used which has received little acceptance. Moreover, in these two studies (82, 58) and in that of Sebastien et al (76), membrane filters used to collect the air samples were subsequently ashed, which introduces some uncertainty in view of the possibility of filter contamination. Our experience has shown that an extensive programme of blank filter measurements must be incorporated whenever filters are ashed. There is no discussion of analyses of blank unused filters in any of these published studies, nor is there any account of the numbers of fibres on which the measurements are based. Precise identification criteria were also not specified, and this is particularly important in view of Spurny and Stober's observation that asbestos fibres represent only 1 - 10% of the total fibre concentration in ambient air (86). These measurements, however, were obtained using the SEM, and in some locations a significant proportion of the fibres could not be identified because they were too small.

Lanting and den Boeft (47) have also used the ashed membrane filter technique to determine asbestos fibre concentrations in industrial and rural towns. These results were somewhat lower than those found in the U.S.A. For example, in large industrial towns, the levels were $0.5 - 2.0 \text{ ng/m}^3$ (or $10^3 - 10^4 \text{ fibres/m}^3$), and in rural towns the values were $0.1 - 0.5 \text{ ng/m}^3$ (up to about 10^3 fibres/m^3). The mass concentrations were computed from the numerical fibre counts. The fibre concentrations were found to be higher in a tunnel carrying heavy traffic, and the conclusion was drawn that the increase was due to a contribution from brake linings. Measurements by Gibbs et al (34) in a remote rural

location yielded values generally between 1 ng/m³ and 26 ng/m³, but with one value of 240 ng/m³. For a rural location these values are significantly higher than those of Lanting and den Boeft, and are comparable with the data of Nicholson et al for New York City. Bruckman and Rubino reported that ambient chrysotile asbestos levels were generally less than 10 ng/m³, both in urban and rural locations (15). Other measurements conducted near toll plazas indicated that levels higher than 10 ng/m³ occurred, and it was concluded that brake lining wear was responsible (15).

In a study conducted in California (42) to determine the asbestos emissions from an asbestos plant, measurements upwind of the source were made to establish the local background values. These measurements were made using the direct carbon-coated Nuclepore filter method, and results were reported in terms of both mass and number. Moreover, analytical background measurements were also reported, but only in terms of mass. The results for the upwind samples are shown in Table 6, and it can be seen that the values ranged between 0.0002 fibre/mL and 0.011 fibre/mL. It should be noted that the high values of numerical fibre concentration do not necessarily coincide with the high values of mass concentration. It should also be appreciated that the highest mass concentration of 171 ng/m³ is based on a count of just 3 fibres. The reported blank filter values were 0.2 ng/m³ and 1.2 ng/m³, and on this basis all of the mass concentrations reported except the two highest values must be regarded as statistically insignificant.

In association with measurements being conducted by ORF during 1980-1981 on the interior atmospheres of buildings, a number of parallel measurements of asbestos concentrations in ambient air were also made. These measurements were used for comparison with the interior values, since the Government of Ontario had not specified any level for indoor airborne asbestos measurements

TABLE 6
STUDY OF CHRYSOTILE ASBESTOS
CONCENTRATIONS UPWIND OF AN ASBESTOS PLANT
(After John et al 1976)⁴²

Date	Chrysotile Fibre Concentration		Number of Fibres Counted
	Fibre Concentration, Fibre/mL (All Fibre Lengths)	Estimated Mass Concentration, ng/m ³	
August 1974	0.002	0.4	7
	<0.0004	N.D.*	0
	0.0004	B.D.L. ⁺	1
	0.001	171	3
November 1974	0.011	48	51
	0.0002	0.3	2
	<0.0003	0.03	1
	<0.0002	B.D.L.	1
	<0.0004	N.D.	0
	<0.0003	B.D.L.	1

* None Detected

⁺ Below Detection Limit

which it would regard as of no concern, although an ambient airborne asbestos guideline had been published. The analysts had been placed in an untenable situation where they were required to perform and interpret measurements intended to allay the fears of the public, yet their interpretation could well be challenged in the future by the very agencies which had the responsibility for regulation. Accordingly, the only realistic approach was for a direct comparison of interior and exterior atmospheres to be made, and for the analytical detection levels to be reduced to the lowest practicable levels. A summary of the data obtained is shown in Table 7, in which locations in Metropolitan Toronto have been separated from other Southern Ontario locations. It can be seen that chrysotile fibre concentrations (all fibre lengths) up to about 45 fibres/litre were found, of which several fibres/litre could have lengths exceeding 5 μm . All of these measurements were made using the direct Nuclepore filter preparation procedure and the identification protocol specified in Section 4.

Recently, in a study conducted for the Royal Commission on Asbestos, ambient air measurements were made at five locations in Ontario, using the direct Nuclepore filter preparation technique and the identification procedures described in Section 4. The results are summarized in Tables 8 - 12. The airborne chrysotile concentrations in all locations amounted to a few thousandths of a fibre/mL. No amphibole fibres were detected. The number of chrysotile fibres counted for each measurement was very low, and most of the values were close to the detection limits. Where large mass concentrations were detected, it was usually found that most of the mass was accounted for by one thick fibre. Although there were few fibres found, it is possible to discern a small difference between the fibre concentrations at the remote rural location (Table 11) and those in Toronto (Table 8). It is clear that the concentrations at the rural location were all below the detection limit. At 95% confidence, the measurements in this location are all lower

TABLE 7

ONTARIO AMBIENT AIR CHRYSOTILE CONCENTRATIONS, 1980-1981

(Measurements made for comparison with values obtained in building atmospheres)

Location	Chrysotile Fibre Concentration*,**			Total Number of Fibres Counted
	Fibres of All Lengths, + Fibre/mL	Fibres Longer Than 5 µm, + Fibre/mL	Estimated Mass Concentration++ (All Fibre Lengths) ng/m ³	
Metropolitan Toronto	0.004	<0.003	0.03	2
	0.006	<0.002	0.03	3
	0.008	<0.002	0.07	6
	0.004	<0.002	0.09	2
	<0.002	<0.002	-	0
	0.004	0.002	0.06	2
	0.019	<0.003	0.20	9
	0.006	<0.002	0.01	3
	0.030	0.004	0.30	8
	<0.002	<0.002	-	0
	0.013	<0.002	0.07	8
	0.045	<0.009	0.16	5
Other Southern Ontario Locations	0.002	<0.002	0.002	1
	<0.002	<0.002	-	0
	<0.002	<0.002	-	0
	<0.002	<0.002	-	0
	0.021	<0.004	0.10	6
	<0.002	<0.002	-	0
	0.003	<0.003	0.003	1
	0.008	<0.002	0.02	5
	0.033	<0.002	0.2	19
	<0.002	<0.002	-	0
	0.007	<0.004	0.02	2
	<0.004	<0.004	-	0

*Identification following protocol described in Section 4.3

**Amphibole concentrations were below analytical detection limits

+Value reported is the mean; when no fibres were detected the value is reported as less than the value equivalent to detection of 1 fibre

++A mass concentration cannot be calculated when no fibres were detected

TABLE 8

AIRBORNE ASBESTOS FIBRE CONCENTRATIONS: TORONTO,
GARDINER EXPRESSWAY AT SHERBOURNE STREET

Sample	Chrysotile Fibre Concentration*,**					Total Number of Fibres Counted
	Fibres of All Lengths, Fibre/mL		Fibres Longer Than 5 µm, Fibre/mL		Estimated Mass Concentration,++ (All Fibre Lengths) ng/m ³	
	Mean ⁺	95% Confidence Interval	Mean ⁺	95% Confidence Interval		
1	-	0.001 - 0.018	-	0 - 0.009	0.03	2
2	-	0.002 - 0.023	-	0 - 0.010	0.02	3
3	-	0.001 - 0.024	-	0 - 0.013	0.02	2
4	-	0.001 - 0.024	-	0 - 0.013	0.08	2
5	-	0 - 0.009	-	0 - 0.006	0.03	1
6	-	0 - 0.019	-	0 - 0.012	0.06	1
7	-	0 - 0.006	-	0 - 0.006	-	0
8	-	0 - 0.013	-	0 - 0.013	-	0
9	-	0.002 - 0.015	-	0 - 0.006	0.06	4
10	-	0 - 0.013	-	0 - 0.013	-	0
11	0.008	0.003 - 0.019	-	0.001 - 0.013	20 ^ψ	6
12	-	0 - 0.013	-	0 - 0.013	-	0

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

⁺ No mean value is reported when fewer than 5 fibres were detected.

⁺⁺ A mass concentration cannot be calculated when no fibres were detected.

^ψ 51% of the mass contributed by 2 fibres

TABLE 9
AIRBORNE ASBESTOS FIBRE CONCENTRATIONS: MISSISSAUGA,
CUSHING ROAD

Sample	Chrysotile Fibre Concentration ^{*,**}					Total Number of Fibres Counted
	Fibres of All Lengths, Fibre/mL		Fibres Longer Than 5 µm, Fibre/mL		Estimated Mass Concentration, ⁺⁺ (All Fibre Lengths) ng/m ³	
	Mean ⁺	95% Confidence Interval	Mean ⁺	95% Confidence Interval		
1	-	0 - 0.002	-	0 - 0.002	-	0
2	-	0 - 0.002	-	0 - 0.002	-	0
3	-	0 - 0.003	-	0 - 0.003	-	0
4	0.004	0.002 - 0.010	-	0 - 0.003	0.02	6
5	-	0 - 0.004	-	0 - 0.004	-	0
6	-	0 - 0.007	-	0 - 0.007	-	0
7	-	0 - 0.011	-	0 - 0.011	-	0
8	-	0 - 0.007	-	0 - 0.004	0.007	2

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

⁺ No mean value is reported when fewer than 5 fibres were detected.

⁺⁺ A mass concentration cannot be calculated when no fibres were detected.

TABLE 10
AIRBORNE ASBESTOS FIBRE CONCENTRATIONS: OAKVILLE,
OSBORNE CRESCENT

Sample	Chrysotile Fibre Concentration*,**					Total Number of Fibres Counted
	Fibres of All Lengths, Fibre/mL		Fibres Longer Than 5 µm, Fibre/mL		Estimated Mass Concentration,++ (All Fibre Lengths) ng/m ³	
	Mean ⁺	95% Confidence Interval	Mean ⁺	95% Confidence Interval		
1	-	0 - 0.008	-	0 - 0.004	0.03	2
2	0.007	0.002 - 0.014	-	0 - 0.004	0.1	7
3	-	0 - 0.004	-	0 - 0.004	-	0
4	-	0 - 0.004	-	0 - 0.002	0.004	2
5	-	0.001 - 0.011	-	0 - 0.008	8 ^ψ	4
6	-	0 - 0.004	-	0 - 0.004	-	0
7	-	0 - 0.005	-	0 - 0.004	0.006	1
8	-	0 - 0.004	-	0 - 0.004	-	0
9	-	0 - 0.004	-	0 - 0.004	-	0
10	-	0 - 0.004	-	0 - 0.002	0.03	2
11	-	0 - 0.002	-	0 - 0.002	-	0
12	-	0 - 0.002	-	0 - 0.002	-	0
13	-	0 - 0.003	-	0 - 0.002	0.001	1

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

⁺ No mean value is reported when fewer than 5 fibres were detected.

⁺⁺ A mass concentration cannot be calculated when no fibres were detected.

^ψ 99.9% of mass contributed by 2 fibres

TABLE 11

AIRBORNE ASBESTOS FIBRE CONCENTRATIONS: REMOTE RURAL,
NEAR BRACEBRIDGE, ONTARIO

Sample	Chrysotile Fibre Concentration,*,**					Total Number of Fibres Counted
	Fibres of All Lengths, Fibre/mL		Fibres Longer Than 5 µm, Fibre/mL		Estimated Mass Concentration,++ (All Fibre Lengths) ng/m ³	
	Mean ⁺	95% Confidence Interval	Mean ⁺	95% Confidence Interval		
1	-	0 - 0.003	-	0 - 0.002	0.008	1
2	-	0 - 0.002	-	0 - 0.002	-	0
3	-	0 - 0.002	-	0 - 0.002	-	0
4	-	0 - 0.003	-	0 - 0.002	0.006	1
5	-	0 - 0.002	-	0 - 0.002	-	0
6	-	0 - 0.002	-	0 - 0.002	-	0
7	-	0 - 0.002	-	0 - 0.002	-	0
8	-	0 - 0.002	-	0 - 0.002	-	0
9	-	0 - 0.002	-	0 - 0.002	-	0
10	-	0 - 0.002	-	0 - 0.002	-	0

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

⁺ No mean value is reported when fewer than 5 fibres were detected.

⁺⁺ A mass concentration cannot be calculated when no fibres were detected.

TABLE 12

AIRBORNE ASBESTOS FIBRE CONCENTRATIONS: PETERBOROUGH,
WELLER STREET

Sample	Chrysotile Fibre Concentration ^{*,**}					Total Number of Fibres Counted
	Fibres of All Lengths, Fibre/mL		Fibres Longer Than 5 µm, Fibre/mL		Estimated Mass Concentration, ⁺⁺ (All Fibre Lengths) ng/m ³	
	Mean ⁺	95% Confidence Interval	Mean ⁺	95% Confidence Interval		
1	-	0 - 0.002	-	0 - 0.002	-	0
2	-	0 - 0.007	-	0 - 0.004	0.2	2
3	-	0 - 0.007	-	0 - 0.004	0.01	2

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

⁺ No mean value is reported when fewer than 5 fibres were detected.

⁺⁺ A mass concentration cannot be calculated when no fibres were detected.

than 3 fibres/litre for fibres of all lengths, and less than 2 fibres/litre for fibres longer than 5 μm .

In this recent study, in addition to the samples collected on Nuclepore filters, parallel air samples were also collected on conventional membrane filters. A limited comparative study has been made using both direct and indirect (ashing) techniques. Two samples from the Toronto location and one sample from a suburban location (Oakville) were studied. The conventional membrane filters were prepared by the ashing technique. The Nuclepore filters were prepared by the direct, carbon-coated replication, procedure and also by an indirect technique. For this indirect preparation, the deposits were washed from the surface of the Nuclepore filters by ultrasonic treatment in double-distilled water. The water was evaporated and the deposits ashed. The residual ash was re-dispersed in double-distilled water and the resulting suspension filtered using a Nuclepore filter which was then prepared for the TEM by the direct procedure. In both indirect preparations, the conditions were selected so as not to break down the fibres, but to allow loosely held aggregates of fibres to be dispersed. This is in contrast to the techniques of Selikoff et al (82), Nicholson et al (58) and Sebastien et al (76), which were deliberately arranged to break down the fibres so that more accurate estimations of their mass concentration could be made. The results of the comparative study are shown in Table 13, and they indicate that both of the ashing techniques often resulted in much larger values for both the numerical and mass concentrations than those obtained by the direct Nuclepore method. Since the Nuclepore filters were not ashed, the increase in fibre concentration obtained by the indirect preparation could not be attributed to contamination from the filter materials. The mass concentrations were found to either increase or decrease, depending on whether large fibres had been over-represented in the original direct analysis result as a consequence of poor counting statistics. The numerical concentrations of those fibres

TABLE 13

AMBIENT AIR SAMPLES: COMPARISON OF RESULTS OBTAINED BY DIRECT AND INDIRECT ANALYTICAL METHODS

Sample	CHRYSOTILE FIBRE CONCENTRATION*,**					
	Fibres/mL (All lengths)		Fibres/mL (Longer than 5 µm)		ng/m ³ (All Fibre Lengths)	
	Direct Preparation	Ashed Preparation	Direct Preparation	Ashed Preparation	Direct Preparation	Ashed Preparation
Toronto 8 ^ψ (Nuclepore Filter)	<0.013	0.18	<0.013	<0.007	-	2
Toronto 8 (Conventional Membrane Filter)	N.A.	0.21	N.A.	0.010	N.A.	80
Toronto 11 ^ψ (Nuclepore Filter)	0.008	0.15	<0.013	0.004	20	3
Toronto 11 (Conventional Membrane Filter)	N.A.	0.067	N.A.	<0.008	N.A.	100
Suburban 2 ^ψ (Nuclepore Filter)	0.007	0.018	<0.004	<0.0009	0.1	0.2
Suburban 2 (Conventional Membrane Filter)	N.A.	0.004	N.A.	<0.002	N.A.	0.05

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

^ψ For the Nuclepore Ashed Preparation, the particulate was washed off the filter with water. The filter itself was not ashed.

N.A. = Not Analyzed: the conventional membrane filters were not analyzed by a direct preparation.

longer than 5 μm were not significantly increased by the use of the indirect preparation methods, but these were in fact all close to the detection limits. It can also be seen that in the suburban location, where there was no known source of airborne asbestos, the fibre number and mass concentration values were low regardless of whether the direct or indirect techniques were used. The values in Table 13 show that the mass concentrations do not correspond at all with either the total numerical fibre concentrations or the concentrations of fibres longer than 5 μm . Although this study is limited, the results reported illustrate the difficulty in comparison of values obtained using different analytical methods.

5.2 Airborne Asbestos Fibre Concentrations in Buildings

The presence of sprayed asbestos insulation in buildings has been found in some circumstances to contribute to the fibre concentrations of the indoor atmospheres. In 1976, Nicholson et al reported that levels of asbestos fibres up to 800 ng/m^3 had been found in office buildings (57). In 1980, the same group reported that in public school buildings levels from 9 ng/m^3 to 1950 ng/m^3 had been detected, with an average of 217 ng/m^3 (58). These levels were significantly higher than the corresponding outside levels, which were in the range 3 to 30 ng/m^3 . Sebastien et al have also reported a study of building atmospheres, in which asbestos fibre concentrations up to 750 ng/m^3 were found (77, 78).

In contrast to the work so far discussed, measurements by ORF in Ontario and Québec building atmospheres have not in general shown concentrations significantly higher than those observed outside. In one extensive study of a large building insulated with a friable mixture containing a high percentage of chrysotile, Chatfield (23) found no values higher than 17 fibres/litre (all

fibre lengths), or 0.2 ng/m^3 in terms of mass concentration calculated from the dimensions of the observed fibres. In this building, 12 of 15 samples were below the detection limit of about 3 fibres/litre. A large number of buildings which contain chrysotile insulation have been studied in Ontario, and the overall conclusion has been that even in the presence of friable insulation of this type, airborne fibre concentrations were always close to the detection limit of a few fibres/litre. Although only a few measurements have been made, it is thought that friable insulation containing amphibole asbestos releases fibres to the atmosphere more readily than the chrysotile-mineral wool type. Moreover, in terms of airborne fibre mass concentration, the larger diameters of amphibole fibres give rise to much higher mass concentration values than is the case with chrysotile fibres.

Some of the concentrations found in the interior atmospheres of public buildings can be interpreted differently, depending on whether the numerical or mass concentration values are used. This is particularly the case for buildings insulated with amphibole asbestos, and is a consequence of the sensitivity of the mass concentration values to the inclusion of a small number of thick fibres. Table 14 shows examples of typical measurements in both chrysotile and amphibole insulated buildings in Ontario. The large mass concentrations of amphibole fibres found in the first example after removal of amosite insulation would incorrectly indicate a severe worsening of the situation. However, the numerical concentrations remained unchanged after removal of the insulation, and were at the level of detection for each sample, when analyzed at an analytical sensitivity of 2 fibres/litre. Typical results are shown for several buildings in which chrysotile-mineral wool insulation was involved. Some small fibres were found at concentrations statistically similar to normal ambient levels in Metropolitan Toronto, but no fibres longer than $5 \mu\text{m}$ were found when samples were examined at

TABLE 14
EXAMPLES OF AIRBORNE ASBESTOS CONCENTRATION MEASUREMENTS
MADE IN BUILDINGS INSULATED WITH ASBESTOS

Type of Insulation	Asbestos Fibre Concentration*			Total Number of Fibres Counted
	Fibres of All Lengths,+ Fibre/mL	Fibres Longer Than 5 µm,+ Fibre/mL	Estimated Mass Concentration ++ (All Fibre Lengths) ng/m ³	
Amosite, Before Removal	0.003	<0.002	2	2
	0.002	<0.002	0.4	1
	0.002	<0.002	0.4	1
Amosite, After Removal	0.002	<0.002	2	1
	0.002	<0.002	30	1
	0.002	<0.002	40	1
Chrysotile, Before Removal	0.007	<0.004	0.01	2
	0.033	<0.004	0.5	10
	0.014	<0.004	0.7	4
	0.006	<0.004	0.03	2
	<0.005	<0.005	-	0
	0.019	<0.004	0.07	6
	0.044	<0.009	0.2	5

* Identification following protocol described in Section 4.3

+Value reported is the mean; when no fibres were detected the value is reported as less than the value equivalent to detection of 1 fibre

++ A mass concentration cannot be calculated when no fibres were detected.

detection levels of a few fibres per litre.

An explanation of the apparent discrepancy between the Canadian studies and those of Sebastien et al and Nicholson et al may lie in the analytical methods used. The Canadian studies were all based on the direct carbon-coated Nuclepore procedure, which involves no manipulation of the sample. When the suspended particulate concentrations are very low, as they were in the buildings studied, it is difficult to challenge the analytical method used on the basis of either fibre loss during preparation or obscuration of fibres by other particulate. In contrast, both the Sebastien et al and the Nicholson et al studies used indirect analytical methods in which steps were taken to break down the fibres as much as possible during the analysis so that better mass estimations could be made. In this type of analysis, a few fibre bundles with large diameters could give rise to high mass measurements, when in fact the original fibre bundles themselves may represent a numerical fibre concentration which is well below the level of detection of a few fibres/litre.

The interpretation of these air sample data in terms of risk estimation is clearly affected by what parameters of an airborne dispersion of fibres are assumed to be the relevant variables which control the incidence of disease. In workplace atmospheres, practically without exception, legislative control is exercised over numerical fibre concentrations, and current medical opinion seems to be that disease is initiated by a single fibre-cell interaction. Accordingly, the numerical fibre concentration, perhaps with some fibre size limitations, appears to be the appropriate parameter for risk estimation in the environmental situation.

5.3 Airborne Asbestos Fibre Concentrations in Subway Systems

Several underground railway systems have been examined for the presence of airborne asbestos fibres. In 1979, Sumner and Wood reported asbestos fibre concentrations in various stations of the Washington D.C. METRO (90). The measurements, however, were made using phase contrast optical microscopy which, as discussed earlier, is quite inappropriate for ambient measurements. Phase contrast fibre counts of less than 5 fibres/m³ were claimed to have been detected in suspended particulate concentrations of higher than 0.7 mg/m³. The sampling was conducted using Nuclepore filters of 8 µm and 0.4 µm pore sizes in sequence, and only the second filter was examined for asbestos fibres. It is clear from other studies that much of the asbestos could have been attached to other particulate, and in ambient atmospheres any asbestos fibres present are usually too small for detection by optical microscopy. The practice of sequential filtering in this way is also a questionable technique, since the increasing loadings of particulate accumulated on the first filter would certainly have increased its collection efficiency during the sampling period.

In 1976-1980, two air sampling studies were conducted in the Toronto Subway System (9, 8). The 1976 samples were collected on conventional membrane filters, and the ashing procedure was used for the analyses. The ashing procedure used was not designed to deliberately break down the fibres. The maximum fibre concentration found was 2.7 fibres/mL, and with one exception the maximum mass concentration was 2500 ng/m³. The exception was a sample for which the calculated mass concentration was 20000 ng/m³, but 88% of the mass was contributed by a single fibre. This illustrates again the difficulty of interpreting data presented in terms of mass concentrations: the values are seriously affected by statistically-invalid contributions from a few large fibres. The 1980 measurements (8) were made using the

direct carbon-coated Nuclepore preparation procedure, and it was found that the results were significantly lower than the 1976 values which were obtained by the ashed filter technique.

In 1981 a study was conducted to compare ambient asbestos fibre concentrations in the Stockholm Subway with those at locations in the city and in the suburbs. The samples were collected on conventional membrane filters and the ashing procedure was used with conditions selected so as not to deliberately break down the fibres. The results are shown in Table 15. The subway results were very much higher than the values obtained in the city and suburban areas. This large difference and the good consistency of the data within each group gives confidence that background contamination of filters was not a problem in this work. The values obtained in the subway were somewhat higher than those found in the Toronto study, but this may be explained by the fact that the Toronto subway is closer to the surface and has a large number of ventilation shafts. Both studies are consistent with a similar study of the London Underground, in which chrysotile fibre concentrations of up to 309 ng/m³ were found (7).

TABLE 15

AMBIENT ASBESTOS CONCENTRATIONS IN THE STOCKHOLM SUBWAY (1981)

Sample	Chrysotile Fibre Concentration ^{*,**}		
	Fibres/mL	Fibres/mL >5 µm	ng/m ³
City Street (6 samples)	0.007 - 0.085	0.001 - 0.003	0.03 - 2.7
Suburban (3 samples)	0.009 - 0.069	0.002 - 0.003	0.04 - 1.3
Subway (4 samples)	11.0 - 21.0	0.10 - 0.12	170 - 430

* Identification following protocol described in Section 4.3

** Amphibole concentrations below analytical detection limits

6. AMBIENT AIR GUIDELINES

A number of administrations have specified guidelines for maximum ambient air concentrations of asbestos. Curiously, there has so far been no discrimination between the values for different varieties of asbestos. The only available information on these guidelines is summarized in Table 16. The current analytical procedures using TEM can achieve analytical sensitivities of 0.001 fibre/mL, leading to detection levels of 0.004 fibre/mL in measurements on relatively clean atmospheres. If the analytical procedures are under good control and all fibres are identified using the defined techniques, the current TEM methods permit measurements to be made which are fundamentally sufficiently sensitive for administration of the current 0.04 fibre/mL Ontario Ministry of the Environment (MOE) guideline. However, more work is urgently required to develop a well-characterized and reference method of analysis which will produce results appropriate for use in risk estimates. None of the available analytical methods has been completely investigated, and many questions remain to be answered regarding their characteristics. Because different analytical procedures are now capable of producing different results, attempts to enforce guidelines would inevitably lead to some controversy if the airborne concentrations were close to the guideline.

TABLE 16

AMBIENT AIR GUIDELINES

State of Connecticut (proposed) - 30 day Average (electron microscopy)	30 ng/m ³ or 30,000 total asbestos fibres/m ³
Province of Ontario - 24 hour Average (electron microscopy) - 30 minute Average (weight)	40 fibres/litre (>5 µm) 5 µg/m ³
Province of British Columbia (optical)	<0.04 fibre/cm ³
West Germany (proposed) (electron microscopy)	1 fibre/litre (>5 µm)
Montreal Urban Community (optical)	0.05 fibre/cm ³
New York City (recommended by Nicholson) (electron microscopy)	100 ng/m ³
France (Conseil Supérieur d'Hygiène Publique de France proposed ambient air quality inside buildings) (electron microscopy)	50 ng/m ³

7. UNRESOLVED ANALYTICAL PROBLEMS

Although the analytical procedures are now under much better control than the literature of several years ago would indicate, there are significant problems in the interpretation of the results. In some circumstances, when used to analyze the same sample, the indirect preparation techniques give higher fibre counts than the direct methods. Table 17 shows a comparison of some results from the Toronto subway, expressed both as numerical and mass concentrations. For every measurement there is an increase of fibre count when the indirect analytical method is in use, and with one exception this increase is also accompanied by a corresponding increase in mass concentration. In this comparison, background filter contamination is not in question, since the ashed preparations were made by washing the particulate from a sector of the filter and ashing the particulate only, rather than by ashing the filter itself. A similar pattern was seen in parallel analyses of ambient air samples, the results of which are shown in Table 13.

The indirect methods have been criticized because of the possibility of fibre breakage by the ultrasonic treatment step, thereby increasing the numerical fibre count. This topic has been addressed by several authors, with variable results (27, 20, 87, 31, 63), and it is possible that the solution may lie in control of the ultrasonic energy used.

In almost all parallel analyses using direct and indirect preparation methods, the mass concentration increases along with the fibre concentration. Therefore, it seems that more asbestos is usually found when the indirect analytical method is in use. On the basis of this observation, the view could certainly be taken that the direct analytical technique actually under-estimates the airborne fibre concentration, regardless of whether numerical or mass units are chosen for the measurement. A partial resolution of this question may be found by a study of the fibre size distributions provided by the

TABLE 17

TORONTO SUBWAY: COMPARISON OF RESULTS OBTAINED BY DIRECT AND INDIRECT ANALYTICAL METHODS

Sample	CHRYSOTILE FIBRE CONCENTRATION*,**							
	Direct Preparation ⁺				Ashed ⁺⁺ Preparation			
	Mean Fibre Concentration Fibres/mL	Estimated Mass Concentration ng/m ³	Number of Fibres Counted		Mean Fibre Concentration Fibres/mL	Estimated Mass Concentration ng/m ³	Number of Fibres Counted	
			All Lengths	Longer Than 5 µm			All Lengths	Longer Than 5 µm
LA39	0.14	14	20	0	2.6	47	99	0
LA47	0.064	0.14	9	0	0.23	15	30	0
SH43	0.072	0.33	8	0	1.3	35	156	2
SH51	0.11	51	15	2	3.0	190	109	2
LA23	0.016	0.17	3	0	0.11	2.5	23	1
LA41	0.013	0.015	2	0	0.17	11	24	0
LA49	0.018	0.043	3	0	0.039	0.24	6	0
QP45	0.025	19	4	0	0.12	1.2	17	0

* Identification following protocol described in Section 4.3

⁺ Data reported in Reference 8

** Amphibole concentrations below analytical detection limits

⁺⁺ Deposit washed from original filter, then ashed

two analytical methods. Table 18 shows a comparison of size distribution results for two of the samples reported in Table 17. It can be seen in Sample SH43 that most of the apparent increase in fibre count is concentrated in fibre sizes below about 1 μm . In Sample LA49 the low result was essentially unchanged by the indirect analysis. Therefore, from the point of view of legislation, which is specified in terms of those fibres longer than 5 μm , the difference between results from the two analytical methods may be much smaller than the total fibre counts would indicate. Indeed, the indirect result may well be the appropriate one to use. Small asbestos fibres have a strong tendency to aggregate with both other fibres and non-fibrous material. In the direct analytical method, these assemblies of material are not included in the result because either the fibres are obscured or it is too difficult to count the number of fibres which are incorporated. Where such obscured and aggregated material is in the majority, a simple count of single fibres may be a serious under-estimate. These aggregates may comprise the majority of the asbestos present, but they may also not be detected in a routine fibre count because such a small area of the filter is examined in the TEM. An essentially zero result could therefore be significantly increased if account were taken of statistically infrequent aggregates not detected on the small area of sample examined. There are obviously unresolved questions regarding the preparation techniques, and more work is required to establish a standard analytical procedure. This task is currently being studied by an ISO working group (ISO/TC147/SC2/WG18 - TC146/SC3/WG1), but this is a voluntary group with no research funding.

A question also remains about the fibrosity of minerals. The current fibre definition (aspect ratio $\geq 3:1$) encompasses particles of many non-asbestos minerals because they cleave into elongated fragments. The problem is particularly serious in the case of the amphiboles, only a few of which are truly fibrous. A large number of mineral products contain a minor proportion of non-fibrous amphiboles such as tremolite or actinolite. The analytical problem is how to distinguish

TABLE 18

TORONTO SUBWAY: FIBRE SIZE DISTRIBUTIONS OF SAMPLES
PREPARED BY DIRECT AND INDIRECT METHODS

Fibre Length Range, μm	Number of Fibres Counted			
	Sample SH43		Sample LA49	
	Direct Preparation	Indirect* Preparation	Direct Preparation	Indirect* Preparation
0.50 - 0.73	4	70	2	4
0.73 - 1.08	1	56	1	1
1.08 - 1.58	1	14	0	1
1.58 - 2.32	0	9	0	0
2.32 - 3.41	2	3	0	0
3.41 - 5.00	0	2	0	0
5.00 - 7.34	0	2	0	0
7.34 - 10.77	0	0	0	0

* For the indirect preparation the deposits were first washed from the filter by ultrasonic treatment in double-distilled water. The water was evaporated and the deposits ashed. The residual ash was then re-dispersed in double-distilled water and the resulting suspension prepared for the TEM by the carbon-coated Nuclepore procedure.

these fragments from fibres of the truly fibrous materials. Attempts have been made to achieve this (97, 18), but currently there is no simple method to discriminate single particles of the fibrous and non-fibrous forms from each other.

More difficult problems are in the area of the biological relevance of the ambient fibre concentration measurements. If the analytical results are expressed in terms of mass concentration, it is not clear how they can be related to risk estimation, particularly in view of the fact that the biological effect is widely considered to be a consequence of interaction between a fibre and a cell. Although Pott (65) and Stanton and Layard (88) have given some guidance by their work on the biological effects of fibres, there is still disagreement about the minimum fibre length which is biologically relevant, particularly when short fibres are the only ones present. If different weightings are to be used to proportion correctly the biological effects of different fibre dimensions, a complete size distribution will be required in order to obtain a risk estimate. In these circumstances, mass concentrations are not the appropriate measurements to be reported, particularly in view of the disproportionate effect which a few thick fibres have on the mass measurement. A further problem exists concerning the minimum size of fibre which should be included in the measurement. Statistically-valid fibre counts cannot be obtained on the longer fibres when a measurement is terminated after 100 - 200 fibres of all lengths have been counted. In addition, the very small fibres, shorter than about 0.5 μm , cannot be identified reliably, but they form a significant proportion of the total number. Accordingly, if no length limits are specified, most of the fibre counting effort is concentrated on the short fibres, at the expense of a statistically-valid measurement of the larger fibres which are generally agreed to be biologically the most significant.

It is clear that more work is required in the area of analytical methods, particularly in the evaluation of specimen preparation

methods for the TEM and in the discrimination between individual fibres originating from fibrous and non-fibrous analogues of the same mineral. A decision is now required from the biologists as to how dose calculations should be made from a fibre count and size distribution. This information is necessary in order that the analyst can design reliable techniques for measurement of the biologically-relevant parameters.

8. RECOMMENDATIONS

It is recommended that airborne asbestos fibre concentrations in both ambient air and the atmospheres of general occupancy buildings should be measured using only transmission electron microscopy. No other currently-available technique has adequate sensitivity or fibre identification capability. Optical fibre counts made using the conventional phase contrast techniques should not be accepted.

In TEM analyses for airborne asbestos fibres, the method of identification should be stated for each fibre reported. The considerations of Section 4 indicate the significant potential for error, particularly in the case of amphibole fibres. In recognition of the high cost of precise fibre identification, economies can be made in many measurements by basing the identification on morphology or other similarities with properly-identified fibres. However, these economies can lead to error, and a record should be made of what identification procedure was followed for each fibre. Successive and possibly conflicting analyses can then be more easily rationalized with the earlier data.

If the Commission finds that only the long fibres are of biological significance, it is recommended that lower length and diameter limits for analysis should also be established. In ambient atmospheres, the short and thin fibres are very much in the majority, and the most economical analyses can be made by concentrating the effort on only the fibres of biological significance.

It is recommended that a lower concentration limit of interest in ambient atmospheres should be established, along with a maximum concentration guideline. These should not necessarily be equivalent to the lowest detectable level, although in Germany this has apparently been the philosophy used. The recommendation in Germany is for an ambient air guideline of 1 fibre/litre (fibres longer than 5 μm); the recommendation is somewhat controversial since an SEM analytical

method is to be specified. (The Ontario ambient air guideline is currently 40 fibres/litre). Other European countries are currently considering levels comparable with the German recommendation. The ISO working group has concluded that pressures in the members' respective countries would not allow acceptance of a level as high as 40 fibres/litre.

It is recommended that reporting of fibre concentrations should be in terms of fibre numbers. The fibre dimensions should also be reported. If the work of Pott (65) and Stanton and Layard (88) is accepted, it is clear that the relevant parameters for estimation of risk are the number concentration and the dimensions of fibres. The mass concentration appears to be an inappropriate parameter, since very large values can be obtained when a minority of the fibres present are of large diameter and of very low carcinogenic potential. The mass concentration also exaggerates the importance of amphibole fibre concentrations relative to chrysotile, because amphibole fibres are generally of larger diameter. Because the early analytical methods incorporated steps thought to cause fibre disintegration, it was considered by some analysts that the mass concentration was the only reliable value which could be reported. It appears now that this is a naïve view of the analytical problem, and that many of these analytical steps may not cause a significant change in the dimensions of the individual fibres, but simply ensure more complete dispersal and separation of aggregates. In effect, therefore, the indirect analytical methods may provide a more realistic measurement from the risk estimation point of view.

It is recommended that an exposure index should be introduced as an additional means of reporting fibre concentrations in the general environment. This would consist of a single numerical value, obtained by weighting each fibre with the best estimate of its carcinogenic potency obtained from sources such as Pott's hypothesis (65). The difficulties of comparison between situations where size distributions are different would be simplified by this procedure, which would be

based on the best information now available concerning the relative toxicity of different sized fibres. The single value of exposure index could then be related to other values obtained for workplace situations for which some epidemiological data are available.

It is recommended that the indirect method of preparation should eventually be used for ambient air measurements where suspended particulate levels are high. However, until filters can be demonstrated to be free of asbestos contamination, the indirect methods involving ashing of a filter do carry a risk that the result may be compromised. Nevertheless, the indirect method of sample preparation offers significant advantages in sample transportation, fibre counting, detection level and operational factors such as sampling conditions. The direct sample preparation method, although simple, seems to be prone to statistical difficulties because of the nature of the particulate being sampled and the small area of filter examined. However, it is currently the most suitable method for monitoring of building atmospheres where the air is relatively clear of suspended particulate. It is clear that much research is still required in this area to characterize properly the two approaches to specimen preparation, particularly as they relate to ambient airborne particulate containing asbestos fibres.

It is recommended that standard samples be prepared for qualification of laboratories performing ambient air analyses. These should be characteristic of various sources of ambient particulate containing asbestos fibres.

It is recommended that research be initiated to establish less expensive methods for monitoring of ambient airborne asbestos concentrations. The current expenditure of labour per sample for routine analysis only is about 10 man hours, leading to a 1983 cost of about \$600 when instrument operation costs are included. Where precise identification of amphibole fibres is required, the costs can be very high, often as much as \$1000 - \$1500 of additional cost per mineral

species identified. It is clear that this is too expensive for routine use in large surveys, and a less expensive screening method is required for routine monitoring. New methods could still be based on TEM, but using automated methods of sample scanning. Alternatively, they could be based on other approaches such as the magnetic alignment - light scattering technique (21, 29).

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Royal Commission on Matters of Health
and Safety Arising from the Use of
Asbestos in Ontario

180 Dundas Street West
22nd Floor
Toronto, Ontario
M5G 1Z8
416/965-1885

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